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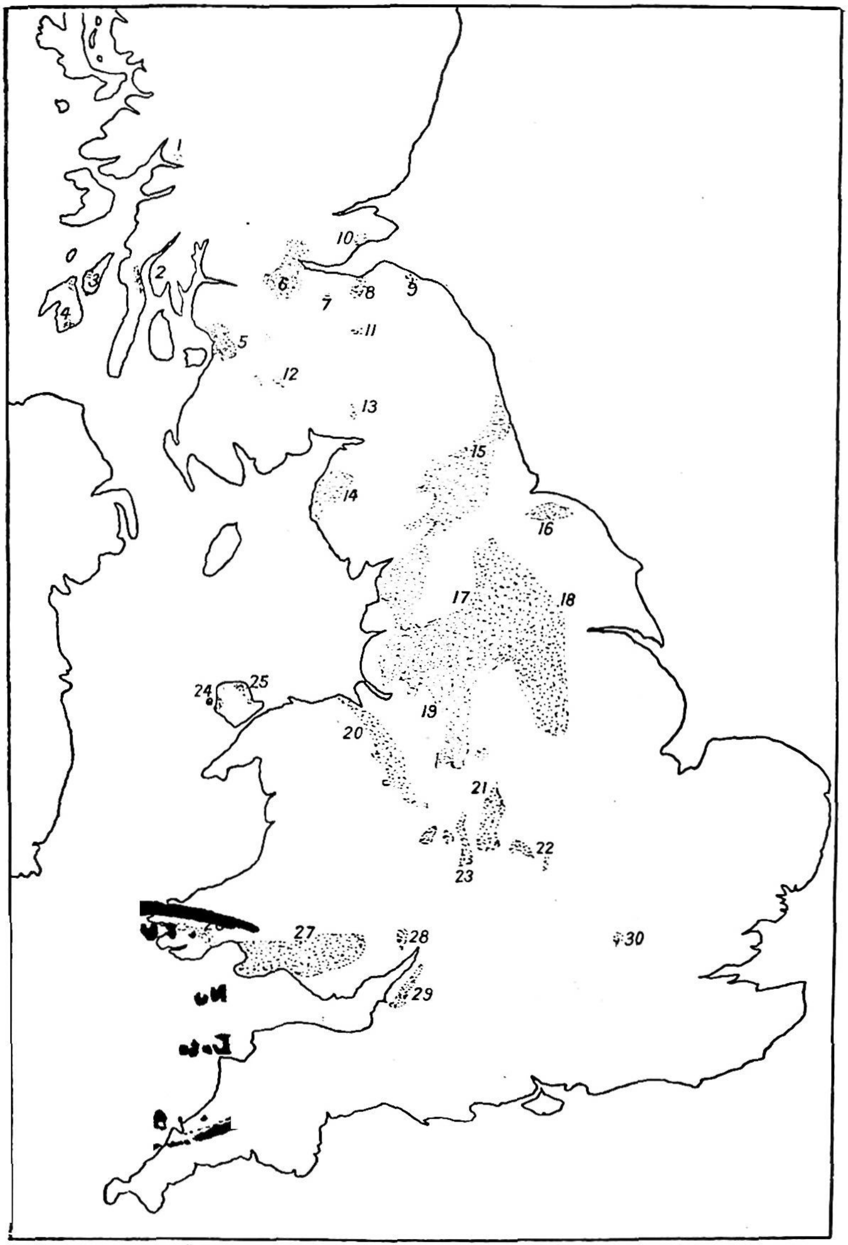

Locations of Siliceous Refractory Materials.

1. Loch Leven.
2. Loch Fyne.
3. Jura.
4. Islay.
5. Ayrshire.
6. Dumbarton.
7. Linlithgow.
8. Edinburgh.
9. Haddington.
10. Fifeshire.
11. Peeblesshire.
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13. Dumfries.
14. Cumberland.
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REFRACTORY MATERIALS:

THEIR MANUFACTURE AND USES.

BY

ALFRED B. SEARLE

CONSULTING EXPERT ON CLAYS AND CLAY PRODUCTS;
LECTURER ON BRICKMAKING UNDER THE CANTOR BEQUEST;
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PREFACE TO THE THIRD EDITION.

THE main purpose of this book—though not the only one—is to assist those engaged in the manufacture of refractory materials to improve their products. Unexpected progress in this respect has been made since the first edition was published, but much still remains to be achieved.

The greatest hopes for future improvements in refractory materials probably depend on:

(i) The recognition that such substances consist essentially of a heat-resisting substance and either a fusible substance or a substance (flux) which can combine chemically with other substances present and so produce a fusible substance.

(ii) The recognition that, as the temperature rises or the time of exposure to a high temperature is prolonged, the amount of fused substance increases, and will, eventually, be present in such a proportion that the material as a whole ceases to resist the action of heat and becomes soft and distorted, or actually melts and drops out of place.

(iii) The recognition that slags and certain other substances (fluxes) react chemically with refractory materials with which they come in contact, thereby increasing the proportion of fused material in the refractory one.

When these facts have been adequately recognised the line of improvement will consist in the selection of:

(*a*) Materials in which the rate of formation of fused material is very slow.

(*b*) Materials which do not readily dissolve in the fusible matter formed during use.

(*c*) Materials with a minimum surface offered to contact with fluxes or abrasives; this implies refractory materials of low porosity.

(*d*) Materials which have been preheated to a much higher temperature than they are likely to attain when in use, so as to prevent any serious change in volume during the period of use.

(*e*) Shapes which can be laid with the thinnest practicable joints.

For most industrial purposes, the bricks and other refractory materials available are quite satisfactory; it is only where the conditions are exceptionally severe (as in steel-melting), when undue regard is paid to first cost, or when an erroneous choice is made, that refractory materials fail to give reasonable satisfaction. The demands of some users are, however, becoming increasingly difficult to meet, and this gives almost unlimited scope for the production of still more highly refractory materials than those now produced on a large scale.

Development in this direction will involve the fundamental study of many materials now used only to a small extent, and the extension of methods of fusion before shaping such as are now employed in the manufacture of electrocast blocks and articles made of silica glass.

The great progress already made and much future progress depend largely on scientific investigation and on individual ingenuity and inventiveness.

Hence, a careful study of scientific journals and of patent specifications is of great importance.

The amount of research work and other sources of information which have been made available since the second edition of this book was published is so large that it is impracticable to include it all, for a text-book must be of a reasonable size and is not an encyclopædia. What to include and what to omit must, necessarily, be largely a matter of individual choice, and for that reason I do not propose to explain why some matters are included and others are mentioned briefly or are omitted. Much that is of great academic or theoretical interest has necessarily had to give place to information of more immediate practical importance, because this book is chiefly used by men in close contact with the actual manufacture of refractory materials.

Like the first edition, this third one has been prepared during the waging of a great war, and the author has been so fully occupied with Government service as to leave little time for attention to some details, which a more leisurely life might have provided; this may be regrettable, but could not be avoided. Detailed references to sources of information have been restricted because they are of use to only a very small proportion of readers, and the space so saved has been used to contain other information of greater value to the majority of readers. Moreover, when an author has been busily engaged in investigations as well as in reading assiduously for more than forty years all the technical and scientific literature of a subject in four languages, as well as innumerable abstracts of papers in other languages, and much of this reading and writing has, perforce, been done away from home (including hotels and railway trains), it is almost impossible, at times, to locate the source of some idea or some information which enters the mind, and if time had been spent in tracking each to its source this edition could not have been prepared. As far as practicable, however, credit has been given to all investigators whose names are known to the author, and any omissions of names are unintentional.

Much information of a confidential nature has necessarily been excluded, as it and many of the results of investigations undertaken by the author for his clients cannot, with propriety, be published.

For much of the work involved in preparing this third edition the author is indebted to numerous friends and to some members of his staff, to whose zealous assistance his thanks are due. He wishes to mention here particularly Messrs. T. Bartholomew, D. S. Hanks and J. Fudge, as well as Miss E. Margaret Smith, who has assisted with the Index. Grateful acknowledgment is also made to firms and individuals who have supplied illustrations and specific information, and also to the Publishers for the exceptional interest shown and the meticulous care taken, together with the shrewd questions raised, which have been a source of pleasure to the author and have aroused the admiration of some of his staff who also are enthusiastic in their interest and attention to details.

The generous reception given to the two previous editions of this book throughout the British Empire and the United States of America, and the many reiterated expressions of regret as soon as the last edition became "out-of-print" encourage the author to hope that in its enlarged and revised form this volume may continue to be of service to all who use it, either as a book of reference or as a text-book.

ALFRED B. SEARLE.

CHARLBURY, OXFORD,
April, 1940.

PREFACE TO THE FIRST EDITION.

THE purpose of the present volume is to summarise, in convenient form, the chief materials and products used in the construction of furnaces, etc., and to describe the manufacture and properties of firebricks, retorts, crucibles, etc., used in the metallurgical, engineering, chemical and other industries. No other book published in this country is devoted solely to this important subject. It is intended to supply the user of refractory materials with the main properties of the materials and products available to him, whilst the manufacturer will also find detailed descriptions of the raw materials, the methods of preparation, manufacture and use. The Appendix contains specifications used by various authorities and sundry tables relating to temperature.

Few people realise that almost every modern industry is dependent on the use of refractory materials. Without them, no steel, brass or other technically valuable metals or alloys could be reduced, no furnaces could be constructed and the use of gas and electricity as sources of power would be impracticable. The wonderful progress which has been made in many other branches of industry during the last three decades would have been impossible in the absence of highly refractory materials.

In order that this progress may continue and be extended to still other industries, it is essential that refractory materials should be studied much more intensely and by a far larger number of people than has hitherto been the case. For example, the production of the highest qualities of optical glass and of the relatively rare elements, such as tungsten, used in the production of special steels, is impeded by lack of materials of sufficient refractoriness, and users of electric furnaces are hampered by their inability to obtain linings which satisfy their exceptionally severe requirements.

Although refractory materials are so essential to industrial progress and development, a search through the Proceedings of the leading Engineering and Metallurgical Societies reveals only a very small number of papers dealing with this subject.

The United Kingdom is particularly rich in excellent fireclays and siliceous rocks and within the British Empire can be found workable deposits of every known refractory material, but their treatment is almost exclusively in the hands of men devoid of the training required to make the best use of these materials. There has, consequently, arisen an idea that little improvement is possible in British refractory materials, with the result that metallurgists, coke-oven manufacturers, gas-engineers and many other users have preferred foreign bricks, retorts, etc., to those made in this country.

It is also a curious fact that, with raw materials inferior to those commonly used in Great Britain, the Belgian, German and Austrian manufacturers have produced goods which are more accurate in shape, less affected by severe conditions of use and generally recognised as being of higher quality than those made here. Moreover, foreign manufacturers have been able to state in detail the properties of their goods under certain conditions and have been willing to guarantee results to an extent which most British manufacturers have found impracticable.

The *economic* reasons for this difference have been discussed in a paper by the author in the *Journal of the Society of Arts* (January 1915) and need not be repeated here. The *technical* reasons are given fully in the present volume. They are concerned with methods of production and sale far more than with the availability of suitable raw materials.

Many attempts have been made by the author and others to rouse British manufacturers from their apathy, but with indifferent results until the Institution of Gas Engineers, at the suggestion of Mr. F. J. Bywater, issued a specification for gas-retorts in 1911, and the outbreak of War in 1914 revealed a state of affairs which could no longer be tolerated. Since then, British manufacturers of refractory materials have made extensive efforts to overcome their former disabilities and to produce firebricks and similar goods which conform to a definite specification, though they still have much to learn. Moreover, the action taken by prominent metallurgists has resulted in several of the leading scientific and technical societies vieing with each other in discussing various aspects of the subject and forming numerous committees to deal with them.

There need be no doubt that, under proper management, selected refractory materials of the British Empire can be made into products certainly as valuable as, and often superior to, those of Central Europe, and the author has, therefore, compared British and German goods with great care on pages 329 and 561.

Users of firebricks and other refractory goods are often lamentably ignorant of the properties required in order that these articles shall prove satisfactory for their particular purpose. They are prone to suppose that high refractoriness is the chief requisite, whereas it is frequently of minor importance! In consequence of this lack of technical knowledge—which is, alas, too often shared by the manufacturers of refractory goods — materials which are quite unsuitable for the purpose are often used, with disastrous results. Experience is constantly showing that local conditions must be studied to the fullest possible extent if satisfaction is to be assured and, for this purpose, the co-operation of the user, the technical expert and the manufacturer is needed. The user and manufacturer look at the subject from opposite points of view and their differences can only be reconciled, in many instances, by means of the services of an expert whose knowledge unites that of both manufacturer and user, yet who is equally independent of both. The manufacturer's salesmen do not usually possess the requisite technical knowledge; their business is to sell the particular goods they have to offer and apart from this their efforts are of no value to their employer.

A customary, and yet extravagant practice, is to use one brand of refractory articles after another until one is found which is regarded as satisfactory. This need not necessarily be the best of those available, as few, if any, scientific tests are made by most users, and price often plays far too important a part in the matter.

It is a fact that almost all the refractory articles offered for sale in this country are good for certain kinds of work, but the manufacturers are often unaware of the purposes for which their goods are most suitable, and they therefore make the mistake of recommending them for entirely different ones.

When a firebrick manufacturer or his agent says that the bricks he offers are " the best on the market " and that they are " suitable for every class of work " and " will withstand the highest temperatures," he is either woefully ignorant or is deliberately deceiving his prospective customer. It is therefore important to ascertain what is meant by such phrases in each individual case and to learn, if possible, the facts on which they are based. In the majority of cases where firebricks prove to be unsatisfactory, the chief cause is due to ignorance of the technical characteristics of the goods on the part of the seller or lack of information as to the properties required by the buyer.

In addition to the information gained in practice as a consultant on clays and refractory materials, the author has, for many years, read all the leading British and foreign scientific and technical papers dealing with these subjects, and a considerable amount of information therein has been included in the present volume. All the relative British patent specifications have been examined, and the leading features of those which, in the author's opinion, are of value have been mentioned. In this connection, it is noteworthy that when identical improvements by different people have been granted letters patent, either the first or the most detailed has been mentioned and the others omitted. A number of patent specifications for improvements in refractory materials describe processes which do not yield materials which are refractory, in the sense in which this term is defined on the first page of the present volume; such specifications have been omitted. Methods of making bricks from spent lime, gas- and soap-wastes, sewage sludge, cinders, scorial and some slags have also been omitted for the same reason.

To facilitate the study of any particular product and to assist those readers whose interest is confined to certain chapters, a small amount of repetition has been regarded as permissible and numerous cross-references have been inserted.

The author is grateful to those firms and individuals who have supplied him with illustrations and information. He has endeavoured to mention their names either beneath the illustrations or in the text, but is well aware that it is not always possible to ascertain the source of every piece of information gathered during a period of twenty years on a subject which is so complex as that of refractory materials. Credit is also given to other investigators as far as their names have been ascertained, though the conditions under which some of the chapters were written preclude such acknowledgment in some cases.

The author's thanks are also due to the various members of his staff who have assisted him with this volume, and particularly to Mr. S. W. Barnes, who has read the proofs and compiled the index.

The manuscript was formally commenced in 1913; it was completed and delivered to the publishers in 1914, but the outbreak of War and, later, a disastrous fire at the printers has delayed its publication. The author has used the opportunity thus created to bring the work up-to-date.

ALFRED B. SEARLE.

SHEFFIELD, *February*, 1917.

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REFRACTORY MATERIALS.

CHAPTER I.

THE RAW MATERIALS.

THE attainment of high temperatures has nowadays become so simple and convenient that their aid is invoked in a large number of engineering processes, and, consequently, considerable interest attaches to the manufacture and preparation of materials which are unaffected by heating to high temperatures.

The term *refractory* is usually defined in dictionaries as meaning that a substance to which it is applied is " difficult to fuse." In technology, however, the term " refractory " usually refers to materials used in the construction of furnaces, flues, crucibles, etc., on account of their resistance to heat when they are subjected to the cutting action of flue gases, the influence of slags and of sudden changes in temperature. Hence, the term " refractoriness " is used in two somewhat different senses—

(*a*) To indicate the resistance of a material to the action of heat, quite apart from any accompanying conditions, such as the effect of the atmosphere in which the material is heated. A perfectly refractory material is wholly unaffected by heating; a less refractory one may either burn away (as coal) or melt (as glass). Fireclays and certain oxides (silica, lime, magnesia, alumina, zirconia, etc.) are highly refractory, and show no signs of losing their shape when heated to temperatures below 1700° C., but their behaviour depends chiefly on the amount of impurities present, as comparatively small proportions of these seriously reduce the refractoriness.

(*b*) To indicate the resistance of a material or article to heat under conditions of use, including the effect of hot gases, flue-dust, abrasion, or corrosion by the contents of the furnaces, etc., which are seldom defined in detail.

The distinction is important, for unless it is understood, many statements in the technical press appear to be highly contradictory; the same material will prove refractory in one furnace, but not so in another, though the maximum temperature is the same in each case. The difference in behaviour is due to differences in the conditions to which the material is exposed; a " clean heat " at a high temperature having far less effect than dust-laden gases at the same temperature. Thus, it frequently happens that bricks are condemned as not being sufficiently refractory when the true defect is their inability to resist abrasion or accidental blows, or to withstand rapid cooling. In such a case, a clay of lower absolute refractoriness (*i.e.* as defined in (*a*) above) may prove more durable than one of the purer clays.

No really satisfactory definition of refractoriness is possible unless the nature of the heat, the rate at which the temperature rises, and the length of time the heating is continued are all included in the definition. Of these, the " nature of the heat " is the most difficult to define and regulate; it has to do with the atmosphere surrounding the refractory material—whether it is oxidising or reducing, clean or contaminated with dust; whether it is constant or irregular in character, and so on.

The commonly accepted idea that the refractoriness of a material may be expressed in terms of temperature alone is entirely erroneous. The statement by a manufacturer that his firebricks " will stand 1760° C." is meaningless unless the conditions are stated.

" Refractoriness," or simple resistance to heat, is merely a special property of certain materials and is no guarantee of their commercial value, as it takes no account of their behaviour when heated in contact with substances which may affect them. This is often overlooked in spite of its great importance.

In the following pages, no material will be regarded as " refractory " which shows any external signs of fusion when heated to a temperature of 1580° C. in a furnace in a wholly oxidising atmosphere, and in such a manner that no flue gases can gain access to the material, the temperature rising during the heating at a rate, as nearly as possible, of 10° C. per minute. Under such conditions, a Seger Cone No. 26 will bend until its apex is almost level with the base.[1] If the temperature is raised more rapidly, or the material to be tested is heated in contact with reducing gases, ashes, dust, or other fluxing materials, the temperature at which it will show signs of fusion will be different from that when it is heated under the " standard " conditions stated above, and no reliable criterion of its refractoriness can be obtained. It should be observed that a material which may be regarded as highly refractory under these conditions may be useless in an industrial furnace where dust and the action of flue gases may create an entirely different set of conditions.

In the broad sense in which the word " refractory " is employed amongst users of furnaces, a clay must, when made into bricks, blocks, or other articles, be able to (1) resist the temperature to which it is likely to be exposed in use; (2) resist any pressure likely to be put upon it by adjacent masonry or by material in the furnace; (3) resist vibration such as may occur in movable furnaces (rotary furnaces, etc.), and any accidental blows, as from a poker or a clinkering iron; (4) resist the slagging action of the contents of the furnace or kiln, where the charges come into contact with the refractory material; (5) resist the cutting and abrasive action of flame and flue-dust with which it may come into contact; (7) expand or contract sufficiently uniformly within conveniently narrow limits. It is also necessary that the clay or mixture used should be sufficiently plastic to enable the desired shapes to be made. The chemical action of the material in adjacent parts of the furnace—as where a course of (basic) magnesite and one of (acid) fireclay bricks lie on each other in an open-hearth furnace—may also require consideration. In special cases, the refractory material may be required to possess certain electrical or thermal insulating or conducting properties.

Few refractory materials fulfil all these requirements under very severe conditions, and the user must, therefore, decide to what extent he will forgo some of the (to him) less important requirements. To a very large extent this method of " compromise " depends upon local circumstances for success, and without full details no satisfactory guidance can be given. It must also

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[1] On the Continent, no clay is considered refractory if, when made into a small three-sided pyramid (strictly, a tetrahedron), whose height is at least four times as great as one side of its base, it bends at a lower temperature than Seger Cone 26, when both are subjected to a steady rise of temperature. In the United States the term *Pyrometric Cone Equivalent* (*P.C.E.*) is used instead of "refractoriness."

be remembered that skilled construction is often equally as important as suitable materials in the construction of furnaces, as badly laid masonry may be unsatisfactory even if made of the most refractory clays.

The word refractory is thus applied to two important and distinct groups of materials: (*a*) those which are resistant to heat in the presence of air, and (*b*) those resistant to chemical actions which occur in consequence of the material being in contact with other substances. Many materials which belong to group (*a*) would be useless under conditions applied to group (*b*). For instance, Dinas silica bricks can, if alone, resist a temperature of 1810° C., but in contact with an alkali or base they are destroyed at a temperature below 1000° C. In the construction of furnaces, crucibles, etc., in which chemical reactions take place, the refractory materials must belong to group (*b*), but, in some instances, the properties required are those in both (*a*) and (*b*) groups.

Engineers frequently make a serious mistake in insisting on materials of the (*a*) group—*i.e.* in specifying simple refractoriness—instead of using those in the (*b*) group—*i.e.* resistance to chemical action at a high temperature.

The *chemical composition* of refractory materials should correspond to the reactions which occur when the material is used. For instance, basic substances should not be heated in refractory articles of an acid or siliceous nature, and *vice versa.* The great diversity of purpose for which refractory materials are used has necessitated their classification according to their behaviour with various reagents,[1] so that, broadly speaking, the materials used for the manufacture of refractory goods are—

1. Acid materials, such as clays (chiefly fireclays); silica in the forms of flint, quartz, sandstone, ganister, etc.
2. Neutral materials, such as chromite, graphite or plumbago.
3. Basic materials, such as bauxite, lime, magnesia, zirconia, etc.

Mixtures of materials from two or more of these groups are sometimes used, and in many cases the materials themselves are far from pure. In such a case, the influence of the various materials on each other, or the impurities of the material as a whole, must be considered when refractory goods are required to possess certain characteristics.

In selecting a refractory material, it must always be remembered that the substances with which the material comes into contact when heated will play an important part in the resistance it offers to heat. Thus, an *acid* refractory material such as silica will be destroyed rapidly if heated in contact with a *base* such as lime. The two will react on each other, forming an entirely fresh compound (a *salt*), which is much less heat-resisting than either the acid or the base taken separately. Similarly, a basic material like magnesia will soon be destroyed if heated in contact with an acid like clay, the amount of fusible matter (salt) formed being dependent on the proportion of base and acid and on the conditions under which they are heated. It is, therefore, useless to expect that a mixture of an acid and a basic refractory material will be as heat-resisting as either of them alone, and it is

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[1] It may be well to remind the reader that all substances may be divided into three groups —acid, neutral, and basic or alkaline—according to their action on substances of known character. The sharp taste and corrosive character of many acids are well known, but these are, so to speak, accidental properties, and the most important characteristic of an acid is that it can combine with bases to form salts. Conversely, a base is a substance which can combine with an acid to form a salt, and a neutral substance is one which does not combine directly with either acids or bases. The conditions under which acids and bases combine with each other depend largely on the particular material under consideration, a high temperature being essential with some materials, whilst others combine directly they are brought into contact with each other, even in the cold.

only possible to increase the refractoriness of any given material by mixing it with one of a neutral character when heated or with a material of a similar nature to that used, but of a greater resistance to heat.

The various refractory materials of commercial importance may now be considered in the order in which they have been given above—

ACID REFRACTORY MATERIALS.

The materials in this, the first group, are all of an essentially acid nature, though this characteristic is not observable until they are strongly heated; in the cold materials it is readily overlooked.

The acid refractory materials require to be heated with a base to at least 700° C. before combination can occur, and with some materials prolonged heating at a temperature of 1200° C. to 1500° C. is necessary. At these high temperatures some decomposition of the original acid occurs in some cases, but the resulting products are all salts, thus showing that the original material was a true acid, notwithstanding the fact that it is devoid of many of the most prominent characteristics of such substances as sulphuric acid or vinegar.

The acid refractory materials may be conveniently divided into two groups—

(*a*) *Clays* or crude *alumino-silicic acids.*
(*b*) *Siliceous materials,* including various forms of *silicic acid* or its anhydride *silica.* Materials in this class often contain a small proportion of clay.

Clays occur in nature in such a variety of forms that it is difficult to devise a simple yet comprehensive definition of the term *clay.* Several definitions—such as "clay is a material produced by the natural disintegration of rocks"—are unsatisfactory because they are equally applicable to sand and to limestone flour, are of limited application and are liable to be misleading. Amongst the other important definitions which have been proposed are the following:—

(1) Clays are compounds of silica and water which may be represented by the formula $SiO_2.xH_2O$, in which part of the H_2O (water) is replaced by alumina (Al_2O_3).
(2) Clays are simple salts produced by the combination of an acid (silica) and a base (alumina), and may be termed "silicates of alumina."
(3) Clays are molecular compounds in which hydrated alumina and silica are feebly combined.
(4) Clays are isomorphous mixtures of hydrated alumina and silica.
(5) Clays are mixtures or "double salts" of silicic and aluminic acids.
(6) Clays are mutually precipitated mixtures of colloidal alumina and colloidal silica.
(7) Clays are alumino-silicic acids analogous to silico-tungstates, arseno-molybdates, phospho-molybdates, etc.

The last theory is apparently the most satisfactory, as it may be used to explain more of the complicated reactions of clays than any of the others. Each of the first five definitions explain only a small proportion of the observed phenomena, whilst the last is able to explain a whole series of facts otherwise inexplicable. For most purposes, the following definition is satisfactory, though by no means complete:—

"A clay is a naturally occurring material whose composition corresponds to that of an alumino-silicic acid, but usually mixed with an indefinite amount of sand and other minerals, the whole producing a mass which becomes plastic when mixed with a suitable quantity of water."

Clays from different sources, which give almost identical results on chemical analysis, behave very differently when heated under the same conditions or when treated in a definite manner with such chemicals as sulphuric acid. This is due to the fact that the ultimate composition of clays as shown by analysis only indicates the constituents present and the proportions in which they occur, but gives no idea as to the arrangement of the atoms in these complex compounds.

That clays possess acid properties at high temperatures and are, therefore, either true acids or are decomposed on heating with the formation of acids, is obvious from their reactions when heated with other substances such as sodium carbonate or lime, when definite salts are produced.

The mode of formation of clays in nature is also an evidence of their acid character, as they are a product of the decomposition of alumino-silicates by the withdrawal of the base (usually potash, but sometimes soda and lime) by means of another acid, in exactly the same way that other acids are formed by the action of an acid on a salt.

Further evidence in support of the idea that a pure clay is a definite chemical compound is the fact that, when purified clays react with alkalies or bases, the salts formed contain alumina and silica in a constant ratio (1 : 2). This implies that the clay as a whole takes part in the chemical reactions involved, whereas if the clay were a mixture of compounds of silica and alumina or even of hydrated silica and alumina, the ratio would almost certainly vary, as it would depend on the affinity of the individual substances for each other. Indeed, it appears almost impossible to explain this constancy of ratio unless the essential constituents of clays are definite chemical compounds. In this connection, it is interesting to compare clays with sands, as both are products of the disintegration of rocks; for, whilst the ratio of alumina to silica varies greatly in the finest particles of sand, it is—considering all things—remarkably constant in the corresponding particles of clay.

Furthermore, the analogy between silicates and alumino-silicates in geological reactions is perfect, and affords another indication that purified clays are definite chemical compounds, viz., alumino-silicic acids.

Another example of the manner in which clays act as acids is in their behaviour with common salt. At a bright red heat they decompose this, forming a fused glassy mass, and liberate hydrochloric acid in almost quantitative amounts. This reaction is made use of in the production of glazed drain-pipes, but it has never been thoroughly investigated in the laboratory, though H. V. Thompson and others have done some valuable preliminary work on it.

There are no fully established syntheses of clay, and it is generally thought that the conditions essential to its formation cannot be obtained on a laboratory scale. On the other hand, J. H. Collins claims to have produced china clay by heating felspar with water under pressure, whilst W. Pukall treated a sodalite with hydrochloric acid and ammonia and obtained a product approaching china clay in properties. Later investigations have thrown doubts on the nature of the product obtained by Collins, and Pukall's product is admittedly not china clay but another alumino-silicic acid. S. R. Scholes (Eng. Pat. 117,755) has found that a material corresponding almost exactly to pure clay in composition and properties can be obtained by fusing a mixture of an alkaline alumino-silicate, such as felspar, with potassium carbonate, boiling the fused mass, passing carbon dioxide through the liquid and removing the soluble salts in solution. This synthetic material, according to Scholes, has been used in the manufacture of articles which have the same properties as those made with a pure natural clay.

Laird and Geller[1] claim that plastic clays which have been calcined at temperatures below 700° C. can be rehydrated and their plasticity largely renewed on heating them in an autoclave with water at 200° C. to 250° C. for eight to forty-eight hours. Clays which have been burned at a higher temperature do not rehydrate so easily.

One thing appears certain—that clays are not "silicates of alumina," as is so often stated in the text-books, because this constitution explains so few of their properties.

Clays may, however, be regarded as alumino-silicic acids more or less contaminated by sand and other impurities. The composition of the alumino-silicic acids which are their chief constituent varies with different clays, some containing more silica than others. In all probability, no simple formula can be applied to the composition of any clay, as their constitution is too complex; but, according to Mellor, it may be assumed that the following are the chief alumino-silicic acids in the refractory clays:—

Alumino-monosilicic acid (allophanic type) . .	$Al_2O_3.\ SiO_2.xH_2O$.
Alumino-disilicic acid (kaolinic type) . . .	$Al_2O_3.2SiO_2.xH_2O$.
Alumino trisilicic acid (natrolitic type) . . .	$Al_2O_3.3SiO_2.xH_2O$.
Alumino-tetrasilicic acid (pyrophyllitic type) . .	$Al_2O_3.4SiO_2.xH_2O$.
Alumino-pentasilicic acid (chabazitic type) . .	$Al_2O_3.5SiO_2.xH_2O$.
Alumino-hexasilicic acid (felspathic type) . .	$Al_2O_3.6SiO_2.xH_2O$.

Obviously, the formulæ given above cannot be applied to all materials which may be known as "clay." They can only be applied to the residue obtained when all, or nearly all, the impurities have been separated from commercial clays. Even then, unfortunately, the analytical figures do not yield small atomic numbers, and even when Si_{12} or Si_{18} is taken as a unit it does not eliminate the fractions entirely. Consequently, it is still impossible to regard all clays as containing *one* essential alumino-silicic acid, as there may be an almost indefinite number of different alumino-silicic acids, the general composition of which may be summarised by one of the foregoing formulæ. Thus, the view that all clays consist essentially of *kaolinite* ($H_4Al_2Si_2O_9$) is no longer tenable, though for many purposes it is convenient to regard them as such. As a matter of fact, kaolinite is only one of an enormous number of alumino-silicic acids many of which are isomeric.

The constitution of clays is peculiarly difficult to study because of the minuteness of the particles, their chemical inactivity at ordinary temperatures, and the presence of inseparable impurities. Good work has been done (and is being continued) by means of the micrographic and chemical examination of the particles after they have been separated according to their different sizes and specific gravities.

The separation of fine clay particles by heavy liquids gives too small a purification to be of great value. Passing the material through a 200-mesh sieve is quite effective for removing the sand and coarser particles, but the silt and more minute particles of impurities cannot be separated in this manner. A much better separation of the impurities may be obtained by *elutriation*, *i.e.* by suspending the particles in water flowing at a definite rate, as this effects a separation which depends partly on the size and partly on the specific

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[1] *Journ. Amer. Cer. Soc.*, 1919, **2**, 828.

gravity of the particles. By this means, almost pure specimens of china clay may be secured, if the rate of flow is sufficiently slow and the elutriation is repeated several times. A still better separation is obtained by the addition of a small amount of an electrolyte (such as sodium carbonate or ammonia) to the water used in the elutriation, as the alkali converts the " clay substance " into a colloidal sol, in which state it will remain indefinitely in suspension, whilst at the same time its viscosity is reduced so that the clay parts more readily from the other particles and enables them to sink more rapidly. Unfortunately, this method has the disadvantage of introducing alkali into the clay ; this complicates the problem, as it is sometimes doubtful whether it is possible to remove it or the salts formed by neutralising it. For practical purposes, the proportion of alkali necessary is so small that its effect on the composition of the clay may be neglected, but this is not the case with strictly scientific investigations.

These methods show clearly the complex mixture composing the coarser particles ; but the finest ones—which are the most important in every way—have hitherto eluded this mode of investigation. Some petrologists have assumed that the finest particles have a similar composition to the coarser ones, but such an assumption appears to rest upon an insufficient foundation to be satisfactory, and is often misleading. Thus, the crude clay dug from the deposits in Cornwall contains felspar, but the commercial china clays derived from it and consisting of the finest particles of clay are free from this felspar.

The usual methods of chemical analysis and synthesis when applied directly to commercial clays do not give much information as to the true chemical constitution of clays, as the commercial materials are so crude and their purification—except within the limits previously mentioned—is at present impracticable.

When either a crude or partially purified clay is fused with sodium carbonate and the product is treated with hydrochloric acid, a complete decomposition of the clay is secured, silica being liberated and soluble aluminium chloride being formed. Unfortunately, however, this reaction is of limited usefulness, as it does not show whether the clay is a highly complex chemical compound or simply a mixture of hydrated silica and alumina. Pukall has investigated the corresponding action of sodium chloride on clay, but has not been able to effect a true synthesis, though his results appear to confirm the view that the kaolin he employed is a definite alumino-silicate.

The author has for several years been engaged in investigating the products formed by heating the finest particles with caustic soda and other hydrates and oxides, used in amounts which are not sufficient to combine with the whole of the clay—the material being kept hot for prolonged periods and allowed to cool very slowly by the use of an electric furnace fitted with a vacuum jacket, which reduces the loss by radiation.

This fractional attack has yielded some very promising results, which confirm the author's previously expressed opinion that many natural fireclays consist essentially of a mixture of various alumino-silicic acids ; but much further work in this direction must be done before the results justify publication. When heated in this manner under identical conditions, clays from different sources yield crystallisable zeolites of entirely different composition, and clays from a single source which have been purified as far as is possible by elutriation, yield several distinct zeolites, according to the relative proportions of clay and soda (or other oxide) employed. These zeolites contain the base in combination with both silica and alumina and are undoubtedly true salts. The proportion of alumina and silica in some is the same as in the purest clays obtainable. Hence, it seems reasonable to conclude that, under some conditions, clays behave as true acids and have the constitution of complex acids.

The constitution of clays is still largely unknown, though X-rays, micropetrological and chemical methods have been extensively used in its investigation.

There are some able investigators who believe that no definite group of substances can be termed " clays ": they hold that the term is a loose and indefinite one unsuitable for scientific purposes and applicable to any plastic earthy material.[1] Between this and the opposite opinion—that all clays are definite compounds—there are many theories each containing a modicum of truth. A brief summary of each of these is impossible; it must suffice to state that clays are now regarded as natural mixtures of two or more substances to which the term " clay mineral " is applied, though it is not applied to such substances as felspar, quartz, calcite, etc., which occur as impurities in clays.

Empirically all clay minerals consist of particles less than 0·010 mm. and many are less than 0·002 mm. The characteristics of clay minerals are:

(1) Their composition.
(2) The minute size of the particles.
(3) The plate-like (flaky) shape of the particles. The crystal symmetry is monoclinic or rhombic pseudo-hexagonal. The plates seldom occur singly—mainly in piles.
(4) The crystal structure consists of layers which may account for the flaky shape.

The chief clay minerals are:

(1) Kaolin group (kaolinite, anauxite, intermediates).
(2) Montmorillonite group (montmorillonite, beidellite, nontronite, intermediates).
(3) Halloysite group (halloysite, metahalloysite).
(4) Mica clay-minerals (sericite, etc.).
(5) Magnesic clay-minerals (sepiolite, attapulgite, etc.).

The micas, chlorites, talc, steatite, brucite, and gibbsite are not usually regarded as clay minerals, but strictly they belong to the same group.

The term " clay minerals " not only includes hydroaluminosilicates, but hydroferrisilicates and magnesium silicates.

The arrangement of the atoms and OH-groups in the clay-minerals is that shown in Table I. (due to Sir William Bragg [2]), in which the thickness of the stacks of sheets (in Ångstrom units [3]) is also shown.

In this table the unit cell of the crystal consists of sheets of atoms packed on one another, each sheet being a rectangle 5·2×8·8 Ångstrom units. The thickness of the cell depends mainly on the number of oxygen or hydroxyl sheets. The numbers attached to the symbols in the table show the number of atoms or OH groups in each sheet. Sir William Bragg has suggested that there are only two groups of *clays*, that *halloysite* is typical of the first group and *montmorillonite* is typical of the second group, and that all clays belong

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[1] This use of the term is probably derived from the Anglo-Saxon word *claeg*, sticky or plastic.

[2] Royal Institution Discourse, 10th November 1937.

[3] One centimetre contains 100,000,000 Ångstrom units, and 1 Ångstrom unit (Å) = 10^{-8} cm.

to one or other of these groups. J. de Lapparent[1] classifies clays in three groups, according to the thickness of the unit cell (*c*) in the crystalline space-lattice as revealed by X-ray analysis.

TABLE I.

Hydrated Silica.	Brucite.	Gibbsite.
4OH	6OH	6OH
4Si	6Mg	4Al
6O	6OH	6OH
Thickness 5·39Å.	Thickness 4·73Å.	Thickness 4·86Å.

Halloysite.	Kaolinite.
6OH	6OH
4Al	4Al
6OH 4OH	4O + 2OH
4Si	4Si
6O	6O
Thickness 10·25Å.	Thickness 7·2Å.

Pyrophyllite.	Montmorillonite.	Mica (Muscovite).
6O	6O	6O
4Si	4Si	3Si+Al
4O+2OH	4O+2OH	4O+2OH
4Al	4Al	4Al
4O+2OH	4O+2OH	4O+2OH
4Si	4Si	3Si+Al
6O	6O	6O
	Water layer or layers	2K
Thickness 9·4Å.	Thickness 9·2–21·4Å.	Thickness 10·0Å.

Clays with c=7Å include kaolinites, anauxites, beidellite, and halloysite.

Clays with c=10Å include pyrophyllite (with the magnesian analogue talc), attapulgite, polygorskite, and their magnesian analogues the sepiolites and bravaisites, which merge into glauconite as the iron-content increases.

Clays with c=14Å include montmorillonite and (with Fe replacing Al) nontronite.

In the *halloysite group* a sheet of gibbsite lies on a sheet of hydrated silica, and in the *montmorillonite group* a sheet of gibbsite is sandwiched between two sheets of hydrated silica, but the middle hydroxyl sheets have been decomposed, four molecules of water being evolved and four atoms of oxygen with two hydroxyl groups being left from each middle sheet. A further distinction between the two groups is that, whereas in the halloysite group the distance separating the successive sheets appears to be small and constant, in the pyrophyllite group the spacing is variable (depending on the degree of hydration) and is relatively large.

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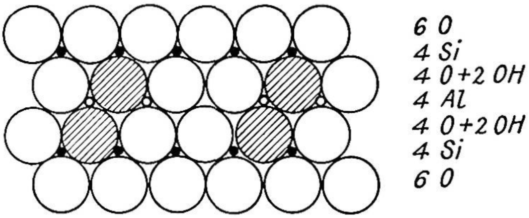
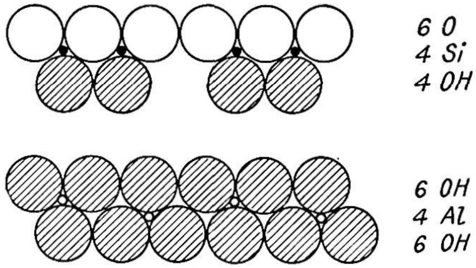
[1] *Zts. Krist.*, 1937, **98**, 233–258.

In these sheets and stacks of sheets, each silicon atom is always surrounded by four oxygen atoms, forming a tetrahedral group (SiO_4). Each oxygen may either be linked to only one silicon, or it may be common to two neighbouring SiO_4 groups which are thus like tetrahedra with a common corner. No two tetrahedra share more than one corner. An oxygen atom linked to only one silicon attracts the cations as if it had unit negative valency. A shared oxygen atom is inert. Aluminium may partly replace silicon in many cases.

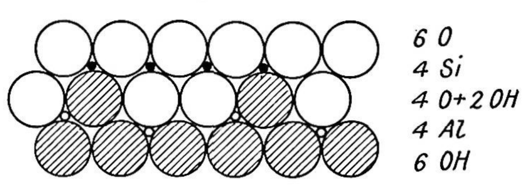
The different types of clay and other silicates are formed by different geometrical ways of linking together the tetrahedra. Thus in olivine,



Pyrophyllite



Halloysite



Kaolinite

FIG. 1.—Structure of clay minerals.

Mg_2SiO_4, the SiO_4 groups are separate. In beryl, $Be_3Al_2Si_6O_{18}$, six tetrahedra are linked in a Si_6O_{18} ring. In the pyroxenes and amphiboles, the tetrahedra are in single or double chains. The acid radicals are thus linear, and are joined sideways by the cations. The tetrahedra can be linked so as to form sheets with infinite extension in two directions in space. Such planar acid radicals build up kaolinite with one silica and one alumina layer, pyrophyllite with one alumina layer and one silica layer on each side; with interposed cations they build up mica and talc. Finally they can build up a three-dimensional structure, which is silica-like except that a part of the silica is replaced by aluminium. These three-dimensional acid radicals have cations in their interstices, and are found in felspar and the zeolites.

In such structures there may be a substitution of Fe or Mg for Al and Fe or Al for Si, because there is room for cations to move freely in and out of the lattice and for base-exchange to occur throughout it.

The attachment of cations (*i.e.* substances which form bases) to clay minerals is different from that in simple chemical compounds, and partial replacements are common.

The uni- and bi-valent bases have been shown by Marshall[1] to fall into four groups, two of which are fixed in the crystal-lattice and two are readily exchangeable.

Group (i). The ions which replace Al in the gibbsite layer—chiefly magnesium.

Group (ii). Cations which balance the negative charge on the lattice, *e.g.* magnesium in the alumina layer, though potassium, sodium, and calcium also occur in a non-exchangeable form.

Group (iii). The cations between the charged layers, in the wide spaces occupied by water molecules. These form the bulk of the exchangeable bases.

Group (iv). A small proportion of the exchangeable cations forms the outer portion of the electrical double layer which surrounds the particles.

The silicon-oxygen framework of the silicates, revealed by X-rays, shows why the complex silicates necessarily only exist as solids; their isomorphous substitution, base exchange, the water content of the zeolites, and many other features are also explained by it. Once in place, the sheets adhere chemically because some of the oxygen atoms act as links, even when others have been eliminated as water. According to Hendricks[2] the water-molecules are arranged in hexagonal networks.

The effect of acids on clays containing small proportions of alkalies or alkali earths is for the acid to combine with the metal ions and remove them in solution and for the corresponding hydrogen ions to take the place of the metal ions in the clay, forming what are known as *H-clays*. If one of these H-clays is washed with a dilute solution of alkali, metal ions will be introduced into the clay—apparently between the sheets—in a very loose state of combination.

The tendency to build up large groups of plates or sheets, arranged face to face, depends largely on the loosely attached hydrogen and metal ions.

The Halloysite Group.—The halloysite group includes *halloysite*, *kaolinite* (kaolin), *dickite*, *nacrite*, *anauxite*, *leverrierite*, and *metahalloysite*. In this group the unit crystalline cell consists of gibbsite overlying hydrated silica (see Table I., p. 9), but from some members of the group some hydrogen and oxygen has been eliminated in the form of water[3] from between the layers of gibbsite and silicic acid. Thus kaolinite appears to have been formed by the elimination of 8 hydrogen atoms and 4 oxygen atoms from a unit of halloysite.

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[1] *J. Soc. Chem. Ind.*, 1935, **54**, 395T.

[2] *Nature*, 1938, **142**, 38.

[3] It must be clearly understood that these atoms do not exist as water in the unit.

$$\begin{array}{lcccc}
6OH & & 6OH & & \\
4Al & & 4Al & & \\
\left.\begin{array}{l}6OH\\4OH\end{array}\right\} & = & 4O+2OH & + & 4H_2O \\
4Si & & 4Si & & \\
6O & & 6O & & \\
\text{Halloysite} & & \text{Kaolinite} & & \text{Water} \\
\text{Thickness } 10{\cdot}25\text{Å} & & \text{Thickness } 7{\cdot}2\text{Å} & & \text{eliminated}
\end{array}$$

It is noteworthy that halloysite appears to be rarer than kaolinite, but as very slight heating appears to convert the former into the latter its relative rarity is not, perhaps, surprising.

In the halloysite group the particles are negatively charged in water, the negative charge being balanced by ions of sodium, calcium and hydrogen in the liquid. Hence cation or base exchange can occur with solutions of salts, acids or bases, but it is restricted to the outer surfaces of the particles, and as the degree of dispersion is low the exchange-capacity is only moderate, even with halloysite.

Kaolinite decomposes and evolves what is known as its " chemically combined water " abruptly at 400–450° C.; halloysite loses it gradually.

(i) *Halloysite*, $Al_2Si_4O_{22}H_{16}$, is the most highly colloidal mineral in this group. It has been found in notable proportions in some Scottish fireclays (p. 57). The contents of a halloysite unit crystal cell may be described by the formula $Al_4Si_4O_{22}H_{16}$ or alternatively as $2Al_2O_3.4SiO_2.8H_2O$, but this latter expression, though convenient, is not accurate, as the molecular forms are not present in the crystalline structure. Some authorities give $Al_2Si_2O_{11}H_8$, but this does not fit the general crystal-lattice. Hendricks (*Nature*, **142**, 38, 1938) gives the formula $(OH)_8Al_4Si_4O_{10}.4H_2O$, which also seems doubtful. Hendricks also claims that hydrated halloysite has only one sheet of water molecules as hydroxyl groups from the bottom of the silicate layer.[1]

Bragg [2] considers that when halloysite is slightly heated its two middle sheets of hydroxyls collapse into one, consisting of four oxygens and two hydroxyls, whilst four oxygens and eight hydrogens are expelled in the form of water. The new form of crystal is metahalloysite; its composition is the same as that of kaolinite. Halloysite differs from kaolinite and metahalloysite only in containing two extra molecules of water, which are so lightly bound that they are expelled at 50° C. The X-ray spectra of halloysite and metahalloysite are very similar, but there is a difference in the crystal-lattice. In some deposits kaolinite appears to have been derived from halloysite.

(ii) *Metahalloysite*, $Al_2O_3.2SiO_2.2H_2O$, is isomeric with halloysite and is formed by keeping the latter at 50° C.[3]

(iii) *Kaolinite*, $Al_2O_3.2SiO_2.2H_2O$, is the chief constituent of kaolin and china clay; it has a great tendency to crystallise, and particles less than $0{\cdot}1\mu$ are scarce. The crystals are monoclinic, $a=5{\cdot}14$Å, $b=8{\cdot}90$Å, $c=14{\cdot}51$Å, $a=100°\ 12'$, and the unit cell contains $Al_8Si_8O_{20}(OH)_{16}$. For the formation of kaolinite from halloysite see *above*.

Kaolinite is white, becomes slightly plastic when wetted and has no

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[1] *Amer. Mineral.*, 1938, **23**, 295.

[2] *Proc. Roy. Inst.*, 1937, **30**, 39–67.

[3] M. Mehmel, *Zts. Krist.*, 1935, **90**, 35.

prominent cleavage. Its specific gravity is 2·6; the hardness is 2–3 on Mohs' scale. Although a clay-mineral, kaolinite is not the dominant constituent of most clays, shales, and soils, and should not be so regarded.

(iv) *Dickite* has the same chemical composition and the same structure as kaolinite. It is only distinguished from it with difficulty. According to Ross and Kerr[1] dickite and nacrite are not found in clays and may not be clay-minerals. They resemble kaolinite, but the layers or sheets are arranged slightly differently (distorted).

(v) *Nacrite* closely resembles kaolinite in composition and crystalline structure, but the unit cell is twice the thickness, a=5·16Å, b=8·93Å, and c=28·66Å; α=91° 43′. The unit cell contains $Al_{16}Si_{16}O_{40}(OH)_{32}$. Its diffraction figure differs from that of kaolinite, though both have the same formula.

(vi) *Anauxite*, $Al_2O_3.3SiO_2.2H_2O$, closely resembles kaolinite, in which some SiO has replaced some AlOH.

(vii) *Leverrierite*, $Al_2O_3.2SiO_2.2H_2O$, appears to be another isomer of kaolinite, which it resembles, but often has a greater alkali and lime content and may be regarded as intermediate between kaolinite and muscovite (mica). It is possibly an intimate mixture of kaolinite and muscovite flakes of extremely small size.[2]

(viii) *Vermiculite*, $(OH)_4Mg_6Si_8O_{20}.8H_2O$, is a clay mineral analogous in structure to halloysite and montmorillonite, and like them composed of sheets formed by joining tetrahedra of oxygen atoms around silicon atoms into interlocked hexagonal groupings[3] combined with octahedra of oxygen atoms and hydroxyl ions about magnesium and aluminium ions.

Vermiculite exfoliates largely when heated and loses its water, increasing in volume to 15–16 times the original. 1 cu. ft. of raw vermiculite weighs 100 lb., but after calcination only 5–10 lb. The raw material is dark coloured, but the calcined product is golden. The largest productive deposit is 7 miles north-east of Libby, Montana, U.S.A., but other deposits are worked in the U.S.A.; it was formed from biotite. It is chiefly used (after calcination) for low-temperature insulation; it is too fusible for use as a general refractory material.

In vermiculite there are two sheets of water molecules between the silicate layers. It differs from other clay-minerals of the halloysite group in having aluminium replaced by magnesium (*cf.* pyrophyllite and talc, p. 16).

In all these minerals the sheet-like construction of the cells permits sheets of water to penetrate, so that plasticity can be developed, though not to the same extent as in the montmorillonite group of clays. Some kaolinic clays, through exposure to water for many ages have, however, been able to retain so much water in sheet form in the unit crystal shell that they become highly plastic, but lose their crystalline properties.

The Montmorillonite Group.—The montmorillonite group of clays consists of a gibbsite structure (AlO_3H_3) sandwiched between two hydrated silica units, but with 16 hydrogen atoms and 8 oxygen atoms eliminated from the two OH groups in the form of water (see Table I., p. 9). This group includes *montmorillonite*, *pyrophyllite*, *boehmite*, *beidellite*, *bentonite*, *nontronite*, and *saponite*.

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[1] *U.S.A. Geol. Survey Prof. Paper* 165E, 1931, 151.

[2] J. de Lapparent, *Compt. rend.*, 1934, **198**, 669.

[3] Hendricks, *Nature*, 1938, **142**, 38.

$$\begin{array}{lclcl}
6O & & 6O & & \\
4Si & & 4Si & & \\
\left.\begin{array}{l}4OH\\6OH\end{array}\right\} & = & 4O+2OH & + & 4H_2O \\
4Al & & 4Al & & \\
\left.\begin{array}{l}6OH\\4OH\end{array}\right\} & = & 4O+2OH & + & 4H_2O \\
4Si & & 4Si & & \\
6O & & 6O & & \\
 & & \begin{array}{c}\text{(water layers)}\\\text{Montmorillonite}\end{array} & & \begin{array}{c}\text{Water}\\\text{(eliminated)}\end{array}
\end{array}$$

The triple sheets in this group are much less firmly bound than the double sheets of the halloysite group; water can penetrate them and increase their distance apart up to 1·5Å without any disruption, but it weakens the structure so that slight mechanical forces greatly increase the degree of dispersion. The colloidal nature of these clay-minerals is usually well developed and particles less than 50 $\mu\mu$ are common.

The sheets are seldom of ideal composition, 3 atoms of Mg readily replacing 2 of Al in the alumina layer without much distortion of the crystal. Similarly, an atom of iron can easily replace one of aluminium.

In the silica layer an atom of aluminium can replace one of silicon, but to make the valencies balance an atom of sodium or potassium or half an atom of Ca or Mg must be incorporated. In the complete structure (see mica in Table I., p. 9) these cations can only find places between the silica and alumina layers, but more loosely attached ions can lie (*a*) between the sheets and (*b*) on the outer surfaces of the stacks of sheets. The positions of these ions cannot be separately determined, but there is evidence that four-fifths of them are in position (*a*). These loosely attached ions are readily displaced and replaced and are the origin of the base-exchange properties of some clays and allied minerals.

If Table I. (p. 9) is correct, many of the older formulæ for minerals in the montmorillonite group are misleading.

According to Ross and Kerr[1] the minerals of the montmorillonite group are completely isomorphous. They are distinguished from the kaolinite group by a higher birefringence (0·03 or higher, as against 0·006 for kaolin minerals). The $Al_2O_3 : SiO_2$ ratio is higher than in kaolinite and they contain other bases, such as Fe_2O_3, MgO, CaO, etc. They have a perfect micaceous cleavage. They are prominent constituents of fuller's earth.

On absorbing water, the crystal-lattice swells in one direction (thickness) and shrinks when the water is expelled by heat. It can remove bases from solution and retain them by absorption and is one of the chief causes of base exchange in clays and zeolites. The following formulæ are often assumed:—

montmorillonite, $Al_2O_3.4SiO_2.nH_2O$;
beidellite, $Al_2O_3.3SiO_2.nH_2O$;
nontronite, $(Al, Fe)_2O_3.3SiO_2H_2O.nH_2O$;

but the composition of these minerals seldom agrees with formulæ; readily replaceable alkalies and bases are often present and some specimens are rich in magnesia.

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[1] *J. Sed. Pet.*, 1931, **1**, 55; *U.S.A. Geol. Survey Prof. Paper* 165E, 1931, 151.

Even the alumina-silica ratio is not constant, though this may be due to cristobalite as an impurity. The water-content also varies greatly.

In this group the surface of the grains is rough—not like kaolin. The maximum refractive index is lengthwise to the cross-section of the flakes. The birefringence is greater than that of kaolinite. The rapid loss of water on heating to 100° C. and the steady loss of water on heating to 500° C. are characteristic of the montmorillonite group. Montmorillonite does not change its X-ray spectrum below 800–1000° C. The water lost below 500° C. must, therefore, be more loosely held than that in kaolinite.

(i) *Montmorillonite* has theoretically the formula $Al_2Si_4O_{24}H_4.nH_2O$ (see Table I., p. 9), but most specimens contain magnesium which partly replaces aluminium, and there is also a small replacement of silicon ions by aluminium and of aluminium ions by iron.

The following formulæ are typical of actual specimens:—

montmorillonite, $Al_2O_3.2{\cdot}8\text{–}6{\cdot}0SiO_2.2{\cdot}4\text{–}7{\cdot}4H_2O$;
magnesic montmorillonite $(Mg, Ca)O.Al_2O_3.5SiO_2.8H_2O$.

It is possible that some minerals regarded as montmorillonite are strictly intermediate between montmorillonite and brucite (MgO_2H_2) or gibbsite ($Al_2O_6H_6$), or are properly to be regarded as montmorillonite interpenetrated with brucite or gibbsite. The refractive indices of montmorillonite and halloysite depend on the water-contents of the materials and so are very variable. When magnesia is present in montmorillonite it also affects the refractive index.

The fact that it has been found in a site where it is being formed[1] by the action of magnesian solutions on plagioclase confirms this and also Noll's synthesis (p. 21). For the present, therefore, the use of the term montmorillonite includes both true montmorillonite, which contains no magnesium, and magnesic montmorillonite, which contains one molecule of magnesia in its formula. For some purposes it is important to ascertain which of these substances is under consideration.

Magnesia-free montmorillonite differs from pyrophyllite only in containing much more " water." As shown in Table I., this is probably in the form of interstitial layers between the sheets in the unit cell. This " water " enlarges the thickness of the crystal unit from $9{\cdot}4\times10^{-8}$ cm. (pyrophyllite) to $9{\cdot}5-21{\cdot}4\times10^{-8}$ cm. (montmorillonite). The density of the mass shows that the added " water " has a specific gravity of nearly 1·3, so that the ions in it are more compressed than in liquid water, but not so close as in some other crystals, in which the " water " is held more tightly. Dry montmorillonite swells when soaked in water. In the swollen condition the total water-content is not a measure of the amount between the layers, as it also includes surface-adsorption. Montmorillonite is fairly common in humid regions. It is often highly colloidal and is negatively charged when suspended in water. According to Hoffmann and Endell, commercial clays do not contain appreciable proportions of montmorillonite.[2] The base-exchange capacity of montmorillonite is high, and this may account for the almost constant presence of magnesia.

Montmorillonite is also a constituent of some bentonites (p. 17) and some fuller's earths. It evolves water continuously when heated up to about 200° C., more slowly at 200°–400° C., and the remainder at 600°–700° C. This difference has been suggested for distinguishing montmorillonite from

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[1] *Amer. Min.*, 1937, **22**, 1124.

[2] *Zts. angew. Chem.*, 1935, **48**, 187.

kaolinite and halloysite; after heating to 500° C. the X-ray pattern of the two latter minerals is destroyed, but that of montmorillonite remains.[1]

An interesting light on its constitution has been shown by J. W. Gruner,[2] who found that when montmorillonite is heated with potassium bicarbonate in a pressure bomb, it is partly converted into felspar (*adularia*) in seven days at 300° C.

(ii) *Pyrophyllite* is commonly assumed to have the formula $Al_2O_3.4SiO_2$ $4H_2O$, but according to Table I. (p. 9) it should contain only one "molecule" of " water." The additional " water " found on analysis is probably present in the form of layers between the sheets; the variability of the proportion present seems to confirm this.

Pyrophyllite does not swell on immersion in water as does montmorillonite. It evolves " combined water " at 400° C. and above and, according to Houldsworth and Cobb (p. 30), it shows two endothermal reactions at 480° C. and 720°–830° C. respectively. The latter is interesting because when pyrophyllite is heated with magnesium chloride to 800° C. it is converted almost quantitatively into cordierite ($2MgO.2Al_2O_3.5SiO_2$) and free silica. On heating to 800° C. with cobalt chloride it forms free silica and cobalt spinel. The product of heating pyrophyllite to 800° C. is $Al_2Si_4O_{10}H$, which is stable up to 1150° C., but above this temperature it decomposes into mullite and cristobalite.[3]

Pyrophyllite closely resembles montmorillonite and has the same crystal structure, but is denser.[4] The unit cell is only 9·1Å thick. Refractive index α 1·552, β 1·558, γ 1·600. The evolution of water on heating is different from that from montmorillonite. Pyrophyllite is analogous to talc, $Mg_3Si_4O_{10}(OH)_2$, but behaves differently when heated, as talc then forms a metasilicate and free silica.

Pyrophyllite is obtainable in commercial quantities in Carolina, U.S.A., where it is used for high-frequency electrical insulators. It is mixed with an organic binder and a " plastic flux " and burned at 1400° C. The burned product is quite white, with a slight gloss; the fractured surface is rough and not at all like porcelain.

(iii) *Boehmite* is present in relatively large proportion in the Ayrshire bauxitic clays.[5] The formula $Al_2O_3.H_2O$ is sometimes attributed to it, but this seems to be incorrect as its properties are those of a clay and not of a hydrated alumina like gibbsite.

(iv) *Beidellite* was formerly regarded as corresponding to the formula $Al_2O_3.3SiO_2.3H_2O$, and more recently to $Al_2O_3.4SiO_2.nH_2O$. The latter is more conformable to the sheet-structure theory explained on p. 9. Beidellite is fairly common in humid regions. It is highly colloidal and when suspended in water it is negatively charged. It has a high base-exchange and is the chief constituent of several bentonites. It has an X-ray spectrum similar to montmorillonite, but differs in other optical properties. In beidellite the predominating replacement is that of silicon ions by aluminium ones, but iron ions may also replace aluminium; when the latter replacement is complete the product is *nontronite*. At present X-ray analysis is unable to distinguish between beidellite and montmorillonite, though their optical properties are different.

[1] Kepper and Aurich, *Sprech.*, 1938, **71**, 307–8.

[2] *Amer. Min.*, 1936, **21**, 511.

[3] Thilo and Schunemann, *Zts. anorg. allg. Chem.*, 1937, **230**, 321

[4] *I.e.* there is less space for water between the sheets.

[5] Lapparent, *Bull. Soc. franç. Min.*, 1935, **58**, 246.

(v) *Bentonite* is a non-plastic material produced from dust of volcanic origin.

The use of the term *bentonite* has been extended from its original application to a specific clay known to occur only in the vicinity of the Black Hills of eastern Wyoming and western South Dakota, and it now includes all clays derived from volcanic ash and comprising chiefly the minerals montmorillonite or beidellite or both.

Bentonites are subdivided into:

(*a*) those which swell greatly when wetted;

(*b*) those which do not swell more than ordinary plastic clays.

Bentonites of the (*a*) group have the remarkable property of increasing greatly the plasticity of clays and other substances to which they are added; this is attributed to the exceptionally large proportion of extremely minute particles in bentonite. This power is greatest when the bentonite contains adsorbed calcium ions; that with sodium ions is less effective. On soaking in water, aqueous solutions or glycerine bentonite swells greatly and is the only substance which swells in all these liquids. It forms true colloidal gels and the absence of plasticity appears to be due to a low consistency in the gels.

The composition is variable, but corresponds roughly to $Al_2O_3.8SiO_2$ $7\text{–}10H_2O$.

Bentonite clays are derived from weathered and altered volcanic ash. The most typical bentonite is found near Belle Fourche, South Dakota, and in eastern Wyoming, but it also occurs in several other States.

Owing to their variable composition, bentonite clays probably form a group rather than a single mineral. Beidellite and boehmite appear to be constituents of such a group.

Sodium bentonites have a high water-content and much wider spacings in the lattice than have calcium or hydrogen bentonites, and their sediment-volumes differ correspondingly.

Acid-washed bentonite with OH groups on the surface instead of alkali or alkaline earth metal ions is still highly dispersed, but after drying it cannot be dispersed again.

In ordinary bentonite the metal ions keep the plates apart on drying and facilitate the re-entry of water later. Some bentonites can be activated by treatment with dilute acids, which greatly increases their adsorbent and decolorising power. Bentonite is thixotropic, *i.e.* a " slip " containing 15 per cent., if left, solidifies and the container can be inverted without spilling the contents. Kaolin does not do this.

Bradley, Grim, and Clark[1] found evidence of four hydrates differing by steps of six water molecules per unit cell and 3Å in the basal spacing. The second hydrate was stable at 95 per cent. relative humidity: the higher hydrates were formed when wet samples were slowly dried.

After being heated and cooled bentonite can absorb water vapour, but kaolin absorbs none. Bentonite[2] absorbs much heat when heated to 100° C., but kaolin only a little.

Halloysite loses its water chiefly above 445° C.; halloysite loses 2 molecules of water at 50°–100° C. (and forms metahalloysite), it loses a little more water at 100°–430° C., and the rest between 430° and 500° C. Bentonite and halloysite lose water when exposed to air dried by sulphuric acid, but

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[1] *Zts. Krist.*, 1937, A, **97**, 216.

[2] G. Keppeler, *Ber. deut. ker. Ges.*, 1938, **19**, 160.

kaolin shows scarcely any such loss. Bentonite loses water steadily up to 520° C. Kaolin loses a little at 100° C., none from 100°–400° C., and the rest between 400° and 500° C. The rapid loss at 445° C. is characteristic of kaolin.

Metabentonite is a compact massive shale derived from volcanic ash in the central and eastern parts of the United States.[1] It is allied to bentonite, but contains more alkali (5–6 per cent.). The name is that of a *rock* not a mineral.

Saponite, $2MgO.3SiO_2.nH_2O$, is regarded as one of the montmorillonite group of clays—mainly because its X-ray diffraction pattern shows it to be isomorphous with montmorillonite.

Nontronite is a mineral or mineral-group corresponding to montmorillonite or to halloysite in which all the aluminium has been replaced by iron ions. Various formulæ for nontronite have been published, but two are most likely to be correct for the pure substance:

(*a*) nontronite derived from halloysite or kaolinite and having the formula $Fe_2O_3.2SiO_2.2H_2O$;

(*b*) nontronite derived from montmorillonite and having the formula $Fe_2O_3.4SiO_2.H_2O$.

Further research is required before these and other materials described as nontronite can be clearly distinguished. The variations in composition are so great that there seems to be a group of nontronites ranging from an aluminosilicate to a ferrosilicate with isomorphous intermediates. Against this is the fact that the (Al, Fe) : SiO_2 ratio varies, but this may be due to silica present as an impurity. Nontronite crystallises in sheets and fibrous bundles. A pleochroism (yellow to green) is usually observable. The other optical properties vary greatly.

According to W. Noll[2] many mineral terms are merely synonyms and the following are no longer needed:—

carnite
newtonite
steinmark
vermiculite
porcelainite
porcelain earth
samian earth
collyrite
tuesite
arcilla
are all kaolinite;

smektite
fuller's earth
bentonite
terre à foulon
are all montmorillonite;

pholerite is dickite;

höferite
morencite
mullerite
faratshite
pinguite
fetlbol
gramenite
hisingerite
are all nontronite.

The Allophanic Group.—The allophanic group contains minerals with the general formula $Al_2O_3.nSiO_2.mH_2O$. Allophane appears to be amorphous and its composition is somewhat indefinite. The term is used for many clay-like substances which cannot be definitely identified. X-ray analysis shows many of these substances to be montmorillonite or other definite clay-minerals.

In addition are certain *amorphous* substances with an $Al_2O_3 : SiO_2$ ratio of ·1 : 1·1–1·8 and a water-content of 30–38 per cent. The "loss of water"

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[1] Ross, *Bull. Amer. Ass. Petrol. Geol.*, 1927, **12**, 143–164.

[2] *Ber. deut. ker. Ges.*, 1938, **19**, 176.

curve shows a gradual loss as in other amorphous substances. The refractive index varies slightly.

Some allophanes contain a little free cristobalite, but no free amorphous alumina.

The Gibbsite Group.—Gibbsite, $Al_2O_3.3H_2O$, though devoid of silica appears to belong to the clay-minerals and is an important constituent of some clays (see pp. 9 and 201).

The Mica Group.—The occurrence of very minute particles of mica (sericite) in clays is so common that some investigators seem to regard it as a clay-mineral. A reference to Table I. (p. 9) shows that mica may be regarded structurally as montmorillonite (or pyrophyllite, which only differs in its water-content) in which two silicon ions have been replaced by two aluminium ions and two potassium ions added to restore the valency balance.

Several minerals in the sericite group differ from mica by containing less alkali and more water and no base-exchange power. In most sericites the base-exchange is rather greater than that of kaolinite and one-quarter that of montmorillonite (bentonite). Mica has no base-exchange unless extremely finely powdered. The X-ray diagrams of the sericite group show an extraordinary resemblance to those of mica. Refractive index=1·570–1·580. Birefringence 0·022–0·030. The sericites differ chemically from mica only in containing rather less alkali and more water. Their composition lies between $K_2Al_4(OH)_4(Si_6Al_2O_{20})$, muscovite, and $KAl_4(OH)_4(Si_7AlO_{20}).nH_2O$. The curve showing loss of water on heating does not resemble that of kaolinite, halloysite or montmorillonite in any way.

Vermiculite[1] is a term applied to a group of micaceous minerals forming soft pliable lamellæ. When heated they evolve water and open out into worm-like piles by exfoliation of the sheets with an increase in volume to twenty-fold that of the original material (see p. 13).

Identification of Clay-minerals.—All the clay-minerals resemble each other in so many respects that it is often extremely difficult to identify or distinguish them.

They may best be distinguished *from other minerals* by:

(i) Their general composition, the chief constituents being aluminium, silicon, oxygen and hydrogen. They differ considerably in the proportions of these constituents, and many minerals which are not clay also consist chiefly of the same elements.

(ii) The smallness of the particles, as all the clay-minerals occur in particles less than 0·01 mm. in diameter.

(iii) The plasticity of the material when mixed with a suitable proportion of water. Plasticity is not always a characteristic of clay-minerals, though formerly it was thought to be their chief property. The plasticity of clays appears to be due to the possession of a high surface-activity as well as a lamellar structure, rather than to their chemical constitution.

(iv) A high shrinkage on drying, but this is not a property of some clay-minerals.

(v) A marked binding power (p. 121), though this is not a characteristic of all clay-minerals. The drying-shrinkage and binding power of most clays seem to be chiefly due to the beidellite or montmorillonite present.

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[1] Care must be taken not to confuse the mineral vermiculite with the portions of china clay which are known as vermiculites (p. 28).

(vi) A characteristic feature of the clay-minerals is that they form a group (or a series of groups) in which large replacements of one metal (cation) by another can occur without serious distortion.

Some of the minerals which form clays (*e.g.* halloysite and beidellite) are *non-reactive, but the bentonite and montmorillonite types have univalent* and bivalent cations as constituents of the lattice and these can undergo base-exchange reactions with the cations of solutions of salts. The dominant bivalent cation within the lattice is magnesium, but calcium is the predominant exchangeable cation. This property of base-exchange is very important in some uses of clay, but is of minor significance in refractory materials. All these minerals appear to owe their peculiar behaviour to their extended acid radicals; the latter cannot be isolated by chemical means as the whole structure breaks down when this is attempted.

The clay-minerals can best be distinguished *from each other* by:

(*a*) The X-ray spectrum, which is highly characteristic of each. X-ray analysis is the most reliable means of distinguishing clay-minerals, though impurities in the form of very minute particles interfere. These impurities interfere much less with the amount of water absorbed by the raw clay and lost on heating, the amount re-absorbed, the thixotropy and the surface-properties (adsorption and plasticity). X-ray analysis alone will not serve to distinguish between some minerals, *e.g.* anauxite and kaolinite, or montmorillonite and beidellite. If the X-ray spectrum of a mixture of kaolinite and montmorillonite is examined before and after heating the material to 500° C., it will be found that the kaolinite lines have disappeared on heating, but those of montmorillonite remain.

(*b*) The refractive index, though this is of little use in distinguishing the impure clay-minerals because the differences are too small.

REFRACTIVE INDEX.

Muscovite	1·56–1·60.
Kaolinite	1·56–1·57.
Halloysite	1·53–1·54.
Metahalloysite	1·55.
Montmorillonite	1·50–1·52.

(*c*) The rates at which they lose " combined water " when heated. These are best shown by means of time-temperature graphs such as figs. 20–22.

(*d*) The temperatures at which the rate of expansion on heating changes, as expansion-temperature graphs of clay-minerals are characteristic.[1] Those for china clay and halloysite are very similar. The graph for beidellite shows an arrest of contraction at 900° C., but otherwise it resembles that of china clay. Sericite clays expand up to 800° C., and then contract very rapidly.

Accurate distinction of clay-minerals from all other substances and from each other is still impracticable though much has been accomplished. Fortunately, these distinctions are of minor practical importance though of great academic interest.

Synthesis of Clays.—The nature of clays—even when they have been freed as much as possible from impurities—is so complex and so little is really known of their structure that it is not surprising that the synthesis or artificial production of clays is still in an undeveloped state. Many attempts

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[1] Hyslop and McMurd, *Trans. Cer. Soc.*, 1938, **37**, 181.

have been made to synthesise clays by decomposing kaolin with alkalies and treating the product with acids, but the results are uncertain.

Other attempts have been made to synthesise clays from alumina, silica and water with more definite results. The chief syntheses have been made by Schwarz and Trageser (*Zts. anorg. allg. Chem.*, 1933, **215,** 190; 1935, **225,** 142), W. Noll (*Zts. Krist.*, 1936, B, **48,** 210; *N. Jahrb. Min.*, A., 1935, **70,** 65; *Chem. Erde*, 1936, **10,** 129; *Nachr. Ges. Gött. math. nat. Kl.*, 1932, 122; *Sprech.*, 1937, **70,** 143), and Ewell and Tusley (*Jour. Res. Nat. Bur. Standards*, 1935, **15,** 173), who have found that:—

Kaolinite can be synthesised:

(1) By heating aluminium hydrate and silicic acid in pure water or in acid or alkaline solution to 300° C. under a pressure of 87 atmos.; in the presence of alkalies some sericite and montmorillonite is formed.

(2) By heating felspar and leucite with a dilute acid up to 350° C. Above 400° C. pyrophyllite is formed.

Dickite can be synthesised by heating aluminium hydrate and silicic acid with water heated to 350°–365° C.

Montmorillonite is synthesised at 300° C. by heating aluminium hydroxide and silicic acid in a solution of alkali or alkaline earth or a carbonate. The best yield is with R_2O or $RO : Al_2O_3 : SiO_2 = 0{\cdot}2 : 1 : 4$. With less alkali, kaolinite is also formed. The presence of magnesia in the solution may not be essential, but it yields the best output. If more than 0·2 molecule of alkali is used kaolin is also formed, and if more than one molecule of alkali, analcime and similar silicates are produced.

Pyrophyllite is synthesised by heating aluminium hydroxide and silicic acid in the molecular ratio 1 : 4 with steam at a temperature above 350° C.

Beidellite was synthesised by heating aluminium hydroxide and silicic acid at 350°–390° C. in the presence of an alkali.

Nontronite was synthesised from ferric hydroxide and silicic acid in the presence of water at 350° C.

These investigators were unable to alter andalusite, cyanite, sillimanite, mullite and pyrophyllite by heating in an autoclave at 350° C. for more than ten days. Owing to the great complexity of the clay-minerals and the difficulty in identifying them, these syntheses must be accepted with some reserve. The best products may be *isomers* of the clay-minerals (*i.e.* substances of the same chemical composition, but having different physical properties and so destitute of the characteristics of the original clay).

Fortunately, the mineralogical structure of the smallest particles of clays is of academic rather than practical interest, though it has a considerable bearing on a proper understanding of plasticity and on the behaviour of clays when heated. Many of the properties of clays are best understood from a consideration of their physical structure.

The Colloidal Nature of Clays.—Quite apart from their ultimate chemical or mineralogical constitution, clays have a physical structure. They consist of a complex of positively and negatively charged ions, in which one of the ions (the cation) is of ordinary molecular or atomic dimensions whilst the other is very large and is of colloidal dimensions. Such substances have the physical properties of colloids, but behave chemically as electrolytes and are conveniently known as *colloidal electrolytes*. Other substances of a similar nature are some of the salts of the higher fatty acids (*soaps*) and humus-complexes.

This physical structure is almost as difficult to comprehend as the chemical constitution. Apart from the coarser particles, chiefly present as impurities, the particles which are characteristic of clays are so complex that it is exceedingly difficult to obtain a satisfactory conception of them, but on the whole they are best pictured as a highly porous core surrounded by a film of glue-like nature which swells when wetted, shrinks when dried, and possesses simultaneously the properties of an adhesive and a lubricant. Such a film is termed colloidal in character, and it possesses certain well-known characteristics. The thickness of this film has never been measured and its actual existence may be questioned, as, under some conditions, all the particles of certain clays appear to be wholly composed of matter in a colloidal state, whilst other clays appear to consist of both colloidal and merely amorphous material.

The existence of matter in the colloidal state was first recognised by Thomas Graham in 1861, but T. Schloesing, in 1872, was the first to definitely report the presence of colloidal matter in clays; since that time numerous other investigations have confirmed the importance of the colloidal properties of some clay particles, and Rohland has concluded that the plasticity, adsorption, shrinkage on drying, resistance to abrasion and chemicals, and semi-permeability of clays are all due to their being colloidal in character.

As in the case of the chemical constitution of clays, so is it with their physical nature, both being of so complex a character that no single theory satisfactorily includes all the known facts. At present three distinct hypotheses all appear to be of value, though none is complete in itself; these are—

(i) Clays are mixtures of inorganic compounds, which have subsequently been reduced to the colloidal state, together with sand and other impurities.

(ii) Clays are mixtures of mutually precipitated colloidal alumina and silica with other substances such as sand, etc. Thus, J. W. Mellor has suggested that clayite is a colloidal variety of kaolinite, and that halloysite, allophane, and some other compounds containing alumina, silica, and water are gels of colloidal alumina and silica hydrates.

(iii) The theory previously mentioned that clays consist of mixtures of more or less inert yet highly porous particles, each surrounded by a film of colloidal matter, sand, etc.

The author prefers the last theory, whilst recognising that both the others explain many of the facts regarding the properties of clay, but no one theory is sufficient to explain the whole of them. This need not be surprising, for it is highly probable that clays in different localities may have been derived from rocks of widely different origins and so may have different constitutions. Thus, china clay is not soluble in hydrochloric acid, whilst the laterite clays of the Deccan in India are very largely soluble; this suggests that the laterite clays may consist of mutually precipitated mixtures of colloidal silica and alumina, whereas the insolubility of the china clay appears to indicate that it is a definite chemical compound.

Some of Rohland's investigations appear to show that the production of colloidal matter in clays has taken place subsequent to their formation; in his opinion, the colloidal matter is produced by the action (hydrolisation) of water or very dilute solutions of alkalies or bases on the clay particles. The fact that the addition of such substances to water greatly increases its power to retain clay in suspension seems to support this theory.

The principal properties of clays which can be attributed to its colloidal nature are—

1. The manner and extent to which moist clays will absorb water.
2. The hydrolysis of clay.
3. The hygroscopicity of dried clay.
4. The dehydration of clays.
5. The miscibility of clay with water and especially with very dilute alkaline solutions.
6. The suspensibility of clay by electrolytes forming " clay slips."
7. The flocculation of clay slips.
8. The " protection " of clay slips.
9. The viscosity of clay slips and its changes under various conditions.
10. The minute size of the particles of clay.
11. The Brownian movement of clays in suspension.
12. The adsorptive power of clays together with the capillary phenomena and semi-permeability which they exhibit.
13. The plasticity, cohesion, and binding power of clays.
14. The effects of " ageing " or " souring " on clays.
15. The migration of particles of clay when in suspension under the influence of an electric current.
16. The unctuousness or greasy " feel."

The hygroscopicity and the minute size of the particles do not necessarily need any special theory to explain them, but the other characteristics mentioned cannot satisfactorily be explained apart from some colloidal theory. In any case, no colloidal theory of clay yet published shows clearly whether the alumino-silicic acids, which may be regarded as the essential " clay substance," are either partially or wholly colloidal or are readily converted into colloidal matter, or whether clays consist essentially of a mixture of colloidal alumina and silica. It is even possible that the colloidal properties are really due to some particular arrangement of the atoms in the clay molecule whereby they combine with water in an unusual manner, but as we can, at present, only surmise on this subject, we must accept the word " colloidal " as expressing certain properties, the true cause of which is not definitely known.

The chief difficulty experienced in formulating a conception of the constitution and structure of clays is due to their great complexity and the difficulty of treating them chemically without destroying their structure.

Thanks to the work of Bragg and others their constitution is being increasingly understood, and it may be summarised with reasonable accuracy in a definition suggested by Endell, Hoffmann, and Wilm[1]: " Clays are hydrous aluminosilicates which crystallise in the same forms as either kaolinite or montmorillonite. The crystals are usually so minute that the mixture of dissociable bases bound to the crystal surfaces reaches measurable dimensions." The crystals are also so small that clay particles have marked colloidal properties and appear to all ordinary means of observation to be amorphous.

Fortunately, the complexity of clays is such that they behave very similarly in many respects notwithstanding their different molecular constitutions, so that as long as the fact that the clays are essentially composed of alumino-silicic acids is borne in mind there is little need to enter very closely into the arrangement of the atoms within each molecule of clay.

For most practical purposes, the physical and not the chemical properties are of chief importance.

Refractory clays occur chiefly in the Coal Measures, but are found in smaller

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[1] *Ber. deut. ker. Ges.*, 1933, **14**, 436.

quantities in other formations. Indeed, there is no sound reason why refractory clays should not occur in all the geological formations in which clays are found, but the quantities of such clays in some formations are so small as to be negligible.

Refractory clays are of two kinds: (1) those containing nearly as much alumina as silica, and (2) those in which the silica largely predominates. The first class includes the china clays (kaolins), some ball clays, and a few Coal Measure fireclays, though the two former are not used for refractory purposes so much in Great Britain as in Germany. The second class includes most of the Coal Measure fireclays, the clays from " pockets " in Mountain Limestone, and various highly siliceous fireclays.

Kaolin is a term applied to all slightly plastic[1] clays of great purity and with a composition very similar to that of china clay, which is the most important member of the series. Originally " Kao-ling " (High Ridge) referred to the hill from which the ancient Chinese obtained their china clay, but at the present time the word is used generally for white-burning, slightly plastic clays found close to the rock from which they appear to have been formed. In France and Germany, a term equivalent to " china clay " is practically unknown, the word " kaolin " being used instead. Care must, however, be taken with regard to the word " kaolin," as it is frequently used for any one of the following substances:—

1. The raw material of any rock containing white clay with other substances.
2. The purified or washed material from such rock (possibly true kaolin).
3. Raw white clays of primary origin, *i.e.* formed *in situ*.
4. Any white " clay " (in this sense it is often erroneously applied to mixtures of clays, etc.).
5. The white decomposition-products of felspars (true kaolin).

In Great Britain, the word " china clay " has quite a definite meaning, as it relates solely to the white clay derived from certain Cornish or Devonian granites. The word " kaolin " should not usually be applied to this material, as the term china clay is preferable except where it is desired to indicate that china clay is only one of a large number of clays all grouped under the more general term " kaolins."

For all ordinary purposes, kaolins may be regarded as identical with china clays in their properties ; some of them have, probably, a somewhat different origin, though this is by no means clearly understood, and most authorities maintain that all kaolins are derived directly from the decomposition of felspar, in spite of some evidence to the contrary, a few kaolins (particularly in America) being distinctly of sedimentary origin. In Great Britain, the larger deposits of kaolin are only represented by Cornish and Devonshire china clays.

There is a strong tendency amongst various writers on clay to employ the term " kaolin " to represent " true clay " or " clay substance." This is by no means a desirable use of the word, and should be avoided. The chief constituent of the purest clays is not " kaolin " (for this, strictly speaking, should refer to the " china-clay rock " or to the whole of the material as it is mined), but is variously described as " clayite," " true clay," and " clay substance." Kaolins are usually prepared from the crude material by careful washing, but in some parts of the world they are found in a sufficient state of purity to be used direct.

The varieties of kaolin are in all probability chiefly due to the rocks from

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[1] In America, some highly plastic clays are also termed *kaolins*.

which they have been formed ; these are not confined to any particular variety of granite as was formerly supposed by Delesse, Andre and Laube, and others. Under suitable conditions of decomposition, almost all felspathic rocks form a white kaolin-like material, and the formation of kaolin from rhyolites, pumice, and glassy materials has been recorded by A. B. Jameson.[1]

If the original rock from which the kaolin has been derived is rich in iron and other impurities, the "kaolin" may also be so impure that it no longer burns white, but buff or red. Such a material is seldom termed "kaolin"; it is more suitably known as primary or residual clay. In Great Britain, however, such clays are rare.

It is extremely difficult to ascertain whether a given sample of kaolin is really pure. As much as 20 per cent. of white mica may sometimes be present without seriously affecting the analysis, and it is only when the investigation is exceptionally thorough that an accurate knowledge of the material may be obtained.

The kaolins, when carefully freed from adventitious minerals, are almost pure alumino-silicic acids, $xH_4Al_2Si_2O_9$, with a composition corresponding very closely to that of the crystalline mineral *kaolinite*. They are of various shades of cream colour when first obtained, the best qualities being a pure white both in the raw state and after prolonged heating to redness. Any colour is largely due to organic matter which is burned out on heating, and to traces of iron compounds which are, to a large extent, removed by the processes of purification adopted by the miners.

The view that kaolin is chiefly composed of crystalline matter (*kaolinite*) is supported by W. H. Bragg's investigations,[2] but the prevailing opinion at the present time is that the precise mineralogical composition of kaolin is unknown. This is not surprising when it is remembered that clay, like sand, is a product of the decomposition of many rocks, and may therefore contain many minerals of extremely similar chemical composition. With slight variations—probably due to the presence of mica even in the purest samples obtainable—kaolins have the composition assigned to pure china clay, viz., silica, 46 per cent.; alumina, 40 per cent.; and water, 14 per cent., corresponding to the formula $H_1Al_2Si_2O_9$. The correspondence is never exact, and unless exceptional care is taken in their purification most kaolins will contain alkalies equivalent to at least 5 per cent. of mica or felspar.

China clay is the only variety of kaolin which occurs in considerable quantities in the United Kingdom. In other parts of the world similar, but not identical, varieties of kaolin are found.[3]

China clay occurs in Cornwall and South Devon in close association with granite, its presence being indicated by a depression in the surface of the ground known locally as a "slade." The china-clay rock does not appear at the surface anywhere in the district, but is generally covered by other materials which may be from 3 feet to 80 feet in thickness and include partially decomposed granite and peat earth. The china clay is very irregularly dispersed amongst the granite, it being almost impossible to assign definite boundaries to the clay areas. It frequently occurs in pockets crossed by numerous schorlaceous veinstones ; hard granite is irregularly scattered through the clay and stanniferous veinstones occur in places.

China clay is generally considered to have been formed by the decomposition

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[1] *New Zealand Journ. Sci. and Tech.*, 1919, pp. 209-219.

[2] See footnote on p. 28.

[3] For information on foreign kaolins, see *A Handbook to the Collection of Kaolin, etc., in the Museum of Practical Geology*, by J. A. Howe (H.M. Stationery Office, 1914).

of the felspar in the granite, as it occurs in a heterogeneous rock which consists of quartz grains, mica, and china clay together with undecomposed granite and small quantities of other minerals such as fluor-spar and tourmaline. The precise manner in which this decomposition has occurred is still open to investigation ; the oldest view that china clay was formed by the gradual weathering of the original rock is not so widely accepted as formerly, and it is now generally agreed that this " kaolinisation," as it is termed, is due to the action of underground water and dissolved gases at an unknown temperature and pressure. Thus, according to Barrow,[1] the china clay found in the granite mass of Bodmin Moor cannot have been produced by weathering, as the mass in which it occurs contains a vast ramifying network of quartz-schorl or " peach," the trunks and branches of which appear to have been ducts and channels along which the hot gases travelled which converted the felspar into kaolin. The brown granite in the same mass is also decomposed, but it is a product of weathering or aqueous action and contains little or no china clay, all the original minerals—even the biotite—being readily recognisable. In other countries, on the contrary, some deposits have clearly been formed by weathering action, including those in Maryland, North Carolina, Pennsylvania, and New Jersey, U.S.A., and in Norway, Denmark, and Carlsbad, Halle, and Meissen, in Germany.

The reactions which occur are so complex as to be only imperfectly understood. Many eminent investigators have endeavoured to represent these reactions by a series of formulæ, but none is really satisfactory.

One of the least objectionable means of representing what occurs is the following:—

	SiO_2.	Al_2O_3.	K_2O.	H_2O.
100 parts of typical orthoclase consist of . . .	64·63	18·49	16·88	..
From this a soluble silicate is removed by water . .	43·05	..	16·88	..
And water is simultaneously added	..	..	..	6·47
The resulting 46·5 parts of kaolin consist of . . .	21·51	18·49	..	6·47

Expressed by formulæ, the decomposition may be represented, according to Fiebelhorn, as taking place after the following manner :—

$$K_2O.Al_2O_3.6SiO_2+2H_2O=Al_2O_3.2SiO_2.2H_2O+K_2O.4SiO_2$$

(Felspar) (Water) (Clay) (Potassium silicate).

W. Pukall[2] has suggested that kaolin is more probably derived from nepheline ($Na_2O.Al_2O_3.2SiO_2$) than from felspar. C. L. Thompson[3] has shown that the reverse reaction occurs when clay is heated with soda, nepheline being formed.

This theory of the formation of pure clay by the decomposition of felspathic rocks is in unison with the decomposition of numerous rocks which is taking place at the present time, though it is extremely difficult to observe the direct formation of clay from felspar.

The foregoing comparison and the use of an equation avoid all reference to the intermediate stages which the orthoclase undergoes during its kaolinisation. What appears to take place is that the granites and porphyries first become porous by the decomposition of the felspar in them, next they fall to

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[1] *Summary of Progress of Geol. Survey,* 1904, p. 27.

[2] *Sprech.,* 1937, **70**, 383, 399.

[3] *Glass Ind.,* 1936, **17**, 265.

powder, and finally produce a clay which is contaminated with undecomposed felspar and undecomposable material such as quartz and some micas.

As may be supposed from a consideration of its origin, china clay in its native state occurs mixed with granite, mica, and free silica. The greater part of these impurities are removed by treating the mixture with water, when they settle out, leaving the clay in suspension. The slurry is afterwards allowed to settle or is treated in a hydro-extractor, and the thick product—resembling porridge—is dried by artificial heat. The resulting product should not contain more than 10 per cent. of materials other than pure china clay. The sum of the lime, magnesia, potash, soda, iron, and titanium oxides will, under such circumstances, not exceed 2 or 3 per cent., the remainder of the impurities being included in the figures for alumina and silica. Thus, the bulk of the impurity is usually *mica*, the smallest particles of which are so small that it is difficult to remove them by any process of washing. This mica is a potassium alumino-silicate, and on analysis its constituents are usually reported as potash, alumina, and silica. Similarly, in a china clay contaminated with 10 per cent. of felspar, only 1·6 per cent. of potash will be introduced by the felspar. In this way, a china clay may appear to be remarkably free from impurities, whereas it may be comparatively impure. This fact is often overlooked in purchasing china clays or kaolins from different dealers.

Some analyses of kaolin and china clays appear scarcely worthy of credence; the best commercial qualities should not differ greatly from [1]—

Silica	45 per cent.
Alumina	39 „
Water	13 „
Other oxides (due to impurities)	3 „

The principal kinds of kaolins and china clay found in commerce are the following:—

Pure kaolins do not contain more than 5 per cent. of free silica and 2 per cent. of fluxes. They are always obtained by washing less pure china clays. After firing, they form a body of milky whiteness.

Alkaline kaolins only differ from the preceding ones in containing a higher proportion of alkalies (derived from felspar (?) and mica), which may reach 5 per cent. The proportion of iron oxide is sometimes 2 per cent. For refractory purposes, they may be purified by very careful washing, which removes the greater part of the felspar and mica and, therefore, the alkalies.

Siliceous kaolins contain a considerable proportion of free silica (quartz) in the state of impalpable powder. The proportion present depends greatly on the care bestowed in the washing, but may reach 20 or even 25 per cent. These clays furnish a body of small plasticity, and are of a light, granular texture. Firebricks made by the Carbis China Clay & Brick Co., from a siliceous china clay, show on analysis: silica 75·7, alumina 20·2, ferric oxide 1·0, lime 0·14, magnesia 0·13, potash 1·76, and soda 0·82 per cent.; they have a refractoriness corresponding to Seger Cone 32.

Alkaline siliceous kaolins partake of the properties of the two preceding kinds, but are less refractory and need not be considered here.

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[1] At least three distinct substances correspond to this analysis and to the formula $Al_2O_3.2SiO_2.2H_2O$, viz. (i) kaolinite; (ii) nacrite; and (iii) an apparently amorphous material for which J. W. Mellor has suggested the term "clayite." The first two are crystalline, kaolinite being optically positive and nacrite optically negative, whilst only the third shows colloidal properties, plasticity, etc., which are characteristic of clays.

Ferruginous kaolins contain so much iron oxide as to prevent them producing an entirely white body. The better qualities of these clays are used for the manufacture of refractory products, if they do not contain too much alkali and iron.

Of these various china clays and kaolins only the inferior grades can be used for firebricks and other refractory goods, as the better qualities are too costly (see Chapter II.).

The physical and chemical properties of china clays and kaolins may be considered as those of the almost pure alumino-silicic acids to which all clays owe their essential characteristics.

The *colour* of kaolins and china clays is white or cream, though some crude kaolins are a very pale grey. The colour of china clays may be considerably modified by the presence of tourmaline, which tends to give it a bluish tinge of greater or less intensity, and by partially decomposed vegetable matter which gives it a grey tone. For refractory purposes, the colour of the raw material is unimportant, except in so far as it indicates the presence of a non-volatile impurity such as oxide of iron. The burned kaolin or china clay should be quite white, though for some purposes a light primrose tint is not objectionable.

The *softness* of kaolins and china clays is very characteristic, as is their particularly unctuous and soapy nature. When rubbed with a piece of bone they take a high polish.

The *plasticity* of these clays is usually low, though some foreign kaolins are highly plastic. When slightly moistened, kaolins and china clays are sticky rather than plastic, and few of them ever develop sufficient plasticity to enable them to be worked alone on a potter's wheel. When mixed with two or three times their volume of water, china clays and kaolins form a milky slurry which requires many hours—in some cases several weeks—before the suspended matter settles and the liquid becomes clear. Some of the finest particles appear to become colloidal, and remain suspended for an indefinite period.

The *texture* of kaolins and china clays is that of immeasurably fine grains consolidated into lumps which can easily be rubbed to powder. To the naked eye china clay appears structureless, but under the microscope it is seen to consist of small flakes or scales, often so minute as to render the identification of their shape a matter of extreme difficulty. A few clearly defined crystals of kaolinite (of the same composition as " clay," $Al_2O_3.2SiO_2.2H_2O$) are usually found. They have a very characteristic arrangement in groups, with a fan-like appearance (*vermiculites*) and like a pile of coins (*rouleaux*). When examined under a microscope by reflected light, these particles have a very pretty pearly lustre. Kaolinite crystals are discriminated from micaceous materials by the former having a lower index of refraction (1·55–1·56), birefringence, and sometimes showing faint polarisation colours under polarised light, though usually being extinguished without colour parallel to the basal plane; basal flakes show a biaxial interference figure.

The bulk of the china clay consists of minute flakes which appear to be amorphous and to correspond to $x(Al_2O_3.2SiO_2.2H_2O)$ in the purest clays, but these are never obtained quite free from iron oxide or alkalies. Owing to their small size and peculiar optical properties, it is extremely difficult to determine directly whether the smallest particles of china clay are amorphous or crystalline,[1] and the ablest investigators are not yet agreed as to the precise

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[1] After an examination of the X-ray spectrum of this material, W. H. Bragg has concluded that it is largely crystalline.

nature of the particles. There is no doubt, however, that in converting kaolin into ware these particles are more active than the visible kaolinite crystals, and the proportion of apparently amorphous particles to crystals must be an important factor in determining the nature of the clay.

Even in the best china clays there are always small needles of blue tourmaline, scales of muscovite, and minute fragments of quartz, though they are much more common in the second-grade clays and in the mica clays. *Tourmaline* is identified by its pleochroism. *Hydromica*, which sometimes occurs, is identified on account of its having single and double refractions greater than kaolinite but less than other micas such as muscovite and sericite. Hydromica seems to represent the transition stage of weathering between sericite and kaolinite. It usually clots together in rouleaux in a similar manner to kaolinite. *Epidote* occasionally occurs, and is recognised by its slightly greenish colour and moderate single and double refractions. Grains of high refractive index and birefringence usually consist of *zircon* or *titanite*, the former being more common and having a lower interference colour than the latter. *Rutile* is readily identified on account of its shape, colour, and refractive properties. Usually it occurs in the form of needles, five or six times as long as they are wide, very clearly cut. It has an interference colour of the first order and the birefringence is very high. *Diaspore*, a hydrated aluminium oxide ($Al_2O_3 . H_2O$) may also occur as orthorhombic prismatic crystals, foliated and scaly forms of a white colour. It may be recognised by its moderately high refractive index and double refraction. It is differentiated from quartz—with which it may be confused—by its greater specific gravity (3·4). *Quartz* is identified by its index of refraction, low interference colours, and lack of cleavage. It is seldom possible to mistake this mineral for some other if in sufficiently large pieces. Smaller particles are less easy to identify on account of their similarity to kaolinite particles. Usually, however, the grains of the former are more angular and it has a more rapid extinction. *Felspar* is seldom found in commercial china clays of British origin.

In a good quality of china clay or kaolin, the whole of the material should pass through a sieve with 200 meshes per linear inch, and at least 90 per cent. should be carried away by a stream of water flowing at the rate of 0·18 mm. per second or 0·43 in. per minute.

China clay should not be affected by dilute hydrochloric acid, but it is decomposed by prolonged treatment with boiling concentrated sulphuric acid.

On drying at 110° C., an ordinary commercial sample loses 10 to 12 per cent. of moisture, and on heating from 300° C. to 800° C. an additional 13 per cent., or about 23 per cent. or more in all. When burned at 1100° C. the best china clay is pure white, very hard, but not at all vitreous, close in texture, and does not readily absorb much water, though to the tongue it feels "porous."

Hodsman and Cobb[1] found that china clay, when heated, has a very small coefficient of expansion up to a temperature of 100° C., increasing largely up to 200° C., and then decreasing and continuing very constant up to 1000° C., the expansion from 0° C. to 1000° C. being 0·53 per cent. Alumina expands rather more rapidly, the relative expansions up to 1000° C. being 8·3 : 10·3. The very small coefficient of expansion of alumina at low temperatures is even more marked than that of kaolin, the steady coefficient continuing from about 150° C. to 1000° C.; the mean percentage expansion from 0° C. to 1000° C. is 0·62.

On heating, china clay is decomposed with the evolution of water, but if a thermo-couple is introduced in the material and the rate at which the

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[1] *Journ. Soc. Glass Tech.*, 1919, 3, 201.

temperature rises is plotted in the form of a graph similar to that shown in fig. 2, prepared by H. Brearley in 1897, it will be seen that the temperature does not rise uniformly but in a peculiar manner. The two marked "kinks" in the curve appear to be characteristic of all true clays, though in impure ones they are less easily recognised. According to Le Chatelier, and later, Mellor and Holdcroft, there is an endothermal (heat-absorbing) reaction at about 500° C., and an exothermal (heat-evolving) reaction at a temperature somewhat above 800° C., but the decomposition appears to occur through a considerable range of temperature.

Houldsworth and Cobb have found that kaolin shows an endothermal reaction from 500° C. to 575° C., and an exothermal reaction from 950° C. to 980° C., and that other alumino-silicates showed reactions at the following temperatures:—

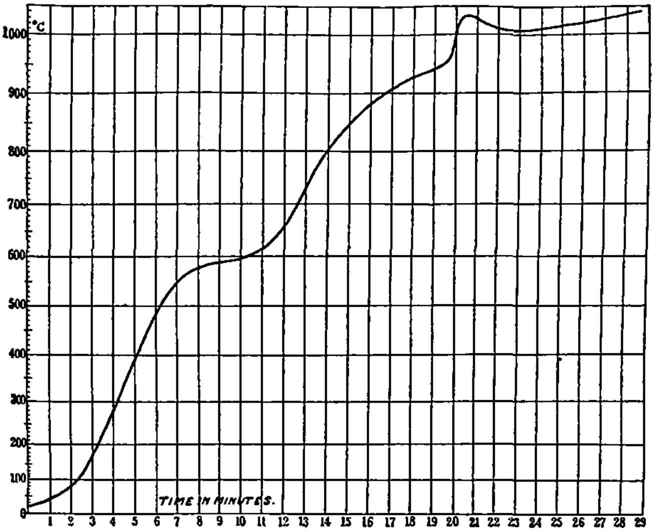

FIG. 2.—Heating curve of china clay.

		Endothermal Reaction.	Exothermal Reaction.
Pyrophyllite		480° C. and 720°–830° C.	
Allophane		50°–140° C., 270°–350° C., 860°–905° C.	950°–970° C. (slight).
Halloysite (?)		50° –130° C., 490°–560° C.	860°–930° C.
Cyanite		775°–850° C.	none.
Andalusite			940° C. (very slight).
Sillimanite	(*a*) Pennsylvania		none.
	(*b*) India	480° C.[2]	950° C.[1]

Mellor and Holdcroft have prepared the corresponding graphs for silica and alumina, and on comparing these with that for china clay they find that there is a kink at 500° C. in both the silica and the clay graphs, and that over the greater part of the range up to nearly 800° C. these two graphs are very similar. On comparing the alumina and clay graphs, Mellor and Holdcroft

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[1] Due, probably, to a little clay present in the sample

find the kink at 800° C. in both, and attribute it to the polymerisation of the alumina. On heating the clay or a mixture of silica and alumina to about 1250° C., there is a further kink (not shown in the illustrations) indicating a further endothermal reaction. Summarising these observations, Mellor and Holdcroft conclude that when china clay (or other clays giving a similar graph) is heated, the decomposition products appear to be free silica, free alumina, and water, the two former only combining after being heated to 1000° C. or above, when mullite ($3Al_2O_3.2SiO_2$) is formed. Mellor, reviewing all the evidence, has stated[1] that only water, free silica and free alumina are formed and that no other theory explains all the facts. The structures shown in Table I. (p. 9) suggest that a complete breakdown would occur on heating and thus confirm Mellor and Holdcroft's theory. X-ray spectrographs taken by W. H. Bragg showed that china clay has a crystalline structure, but after heating to 600° C. it becomes amorphous; this shows that the clay is decomposed, but does not indicate the constitution of the products.

China clays have no sharply defined melting-point. Even minute particles of this clay do not become fluid at any clearly defined temperature, but the material has a semi-molten appearance. For all practical purposes, the purest china clay may be regarded as infusible, its softening temperature corresponding to that of Seger Cone 35 or 36. It does not vitrify appreciably. If either lime or silica be added to pure china clay, in any proportion, the melting-point of the mixture is lowered. On account of the impurities present, commercial china clays usually correspond in refractoriness to Seger Cone 34 or 35, but occasionally a sample is found which is somewhat more refractory. These figures are only applicable to china clay made into pieces the size and shape of Seger cones. Larger masses, such as bricks, have a much higher refractoriness on account of the slow rate at which heat penetrates the mass. The effect of fusing china clay with other substances is described on pp. 32 to 39.

Notwithstanding its whiteness and heat-resisting powers, china clay can only be used to a limited extent in the manufacture of refractory goods on account of its low plasticity, which makes it difficult to manipulate. This difficulty may be overcome by the addition of a plastic clay—such as Dorset or Devon ball clay—but only at the expense of some heat-resistance.

China clay alone is also unsatisfactory for making furnace linings, etc., because of its lack of cohesion, as goods made of it cannot long resist repeated heating and cooling and the corrosive action of dust and other materials with which it comes into contact.

The *quality* of china clay may be ascertained from (*a*) its chemical composition (especially its freedom from iron and alkalies), (*b*) its colour before and after burning, (*c*) its softening temperature when heated, (*d*) its strength, and (*e*) its appearance when freshly cut with a knife. The tints in some samples are commonly due to staining by oxide of iron, but minute particles of other minerals, such as tourmaline or pale mica, impart faint tints to the less marketable products, which are consequently limited in their application, though useful for increasing the refractoriness of a material composed largely of plastic clay. Inferior qualities of china clay and some of the residues from the purification plant are suitable for the manufacture of firebricks.

No definitely satisfactory method of determining the proportions of minerals other than clay in china clay has yet been published. That suggested by Seger, and largely adopted, of boiling the material for fifteen or eighteen hours with sulphuric acid (" rational analysis ") never yields a pure product,

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[1] *Trans. Cer. Soc.*, 1938, **37**, 118.

the "clay" portion invariably containing iron oxide and other bases. For this reason, the author has for many years preferred to follow Fresenius' suggestion, and to regard all the bases other than alumina present in the material as in the form of mica, and to deduct from the ordinary results of analysis the figures corresponding to this assumption. Any remaining alumina is calculated to "true clay" (corresponding to the formula $Al_2O_3.2SiO_2.2H_2O$), and any silica not required by this "true clay" and by the "mica" is set down as "free quartz."

Whilst this method is open to several objections,[1] it is much simpler and freer from defects than the "rational analysis" as ordinarily carried out. Even when the bulk of the foreign mineral does not consist of mica, the results of this calculation are not seriously in error if a note is added to the analysis explaining that the term "mica" in this instance is used to include a variety of silicates other than clay and of somewhat indefinite composition.

The greatest difficulty arises in connection with the iron oxides present in the material. On treatment with boiling sulphuric acid practically the whole of the iron is dissolved and so is included in the figure for "clay substance." To do this is unsatisfactory, and to consider the iron as existing in the form of oxide is equally unsatisfactory, as silicates containing iron are so frequently found in clays.

At the present time the most direct way out of the difficulty—though by no means theoretically satisfactory—is to add together all the bases except iron oxide and alumina and calculate them to mica,[2] as above suggested, and to report the percentage of iron oxide separately. In some cases, however, a microscopical examination will show that the iron is in the form of a definite mineral, such as *siderite,* when it may be reported as such.

To those who possess the necessary manipulative skill, the author can recommend an ingenious method, devised by Allan B. Dick,[3] consisting in mixing a minute portion of the clay with a drop of oil of a refractive index of 1·563 and examining the preparation under a microscope with dark ground illumination, the light being supplied by a mercury vapour lamp, and passed through a yellow glass to approximate the sodium light. If the clay and oil have the same refractive index, the clay particles will be invisible, but mica and other minerals will readily be seen. By changing the temperature of the oil its refractive index is altered, and the other minerals are made invisible in turn. Similarly, by the use of oils of different refractive indices, the proportion of each mineral can be ascertained with fair accuracy.

The *impurities* in commercial kaolins and china clay are usually present in very small proportions; they have generally been removed by the treatment which the material undergoes before it is offered for sale. The most important impurities are *felspar* (seldom found in china clay, but frequently in other kaolins) and *mica.* All these materials are derived in varying quantity from the rock from which the clay was formed and may be identified and their proportions approximately estimated by means of the microscope. The mica is chiefly in the form of muscovite or its decomposition products such as lepidolite or gilbertite; biotite mica occurs only rarely. Both felspar and mica reduce the heat-resisting power of the clay. Quartz is also present in Cornish china clays, the particles being of various sizes from the finest flakes to coarser grains which are easily separated. As stated above, the amount of

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[1] Particularly to the one that true clays may contain widely differing percentages of combined silica.

[2] A microscopical examination will show whether felspar or mica, or both, are present.

[3] See the volume mentioned in the footnote on p. 25.

these impurities may be determined by microscopical analysis, but a more satisfactory test is to heat a small piece of the clay slowly [1] alongside Seger Cone 35. If the sample shows no external signs of fusion when the Seger cone bends, it may be regarded as sufficiently pure for all refractory purposes. For some purposes, an inferior clay which will only stand a similar comparison with Seger Cone 32 is sufficiently refractory.

When a pure clay is mixed with other substances its refractoriness is almost invariably reduced.[2] This is often due to the formation of a compound of the clay and the added substance, such compound being more fusible than either the clay or the added material. The most fusible portion of a series of mixtures of two substances in different proportions is known as an *eutectic*. Its existence may be most readily detected by making a series of mixtures of the desired materials and determining their melting-points. The results are then plotted on a chart so as to form a *graph*, the curved line of which will at once enable the approximate composition and melting-point of the eutectic to be determined, as the eutectic is the lowest point of the graph.

When two definite chemical compounds are mixed, fused, and the molten mass allowed to cool, the first substance to solidify or crystallise is that constituent which has the highest melting-point. When a point is reached in which the composition of the solid portion is the same as that of the still molten mass, the eutectic temperature is reached and only the eutectic can crystallise.

The study of the eutectic of mixtures of two simple chemical compounds is a comparatively easy matter, but with such compounds as clay it is often extremely difficult to draw correct conclusions as to the nature of the eutectics, as the decomposition of the clay may result in the formation of a highly complex mixture. The matter is still further complicated by the difficulty experienced in observing the true temperature of fusion.

Sometimes two or more eutectics may be formed if the substances mixed together are very complex; in this case the graph will show two or more well-marked "lowest points." Clays do not show the formation of an eutectic with some substances, but the melting-points of the mixtures gradually fall so that the graph is a simple curve (fig. 3),[3] or even a straight line. When this is the case it is understood that no definite compound between the clay and the added material is produced. It will thus be seen that the study of the melting-points of a series of mixtures of clay with other substances often gives very valuable information as to the behaviour of the clay under certain industrial conditions, as well as showing the effect of impurities on the refractoriness of the clay.[4]

Some of the impurities in the purest clays may be in the form of substitution products in the atoms forming the clay molecule, particularly those atoms which do not form part of the main groups. Thus, in any of the formulæ given on p. 9 or p. 10 one or more hydrogen atoms may be replaced by a corresponding number of atoms of potassium, sodium, calcium, barium, magnesium, iron, etc.; one or more aluminium atoms may be replaced by an equal number of iron, manganese, chromium, cobalt, etc., atoms; one or more silicon atoms may be replaced by titanium, zirconium, etc. By such replacements (very small

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[1] See p. 2.

[2] The subjects of equilibrium and phase diagrams of clays at high temperatures are more fully discussed in the author's *Chemistry and Physics of Clays and Other Ceramic Materials* (Ernest Benn, Ltd.).

[3] The change in the direction of the curve at Seger Cone 31 is scarcely sharp enough to indicate a definite eutectic or other chemical compound.

[4] See pp. 91 to 94.

in proportion to the weight of the clay [1]) changes would be made in the nature of the material which are out of all proportion to its percentage composition. The action of the replacing atoms will also vary with their nature, base-forming atoms having an effect different from acid-forming atoms, and so on. The possibility that some of the chief properties of clays may be due to the replacement of a small percentage of hydrogen by a corresponding amount of metal does not appear to have received the attention it deserves. This is partly due to the custom of reporting the percentage of alkalies without actually determining it.

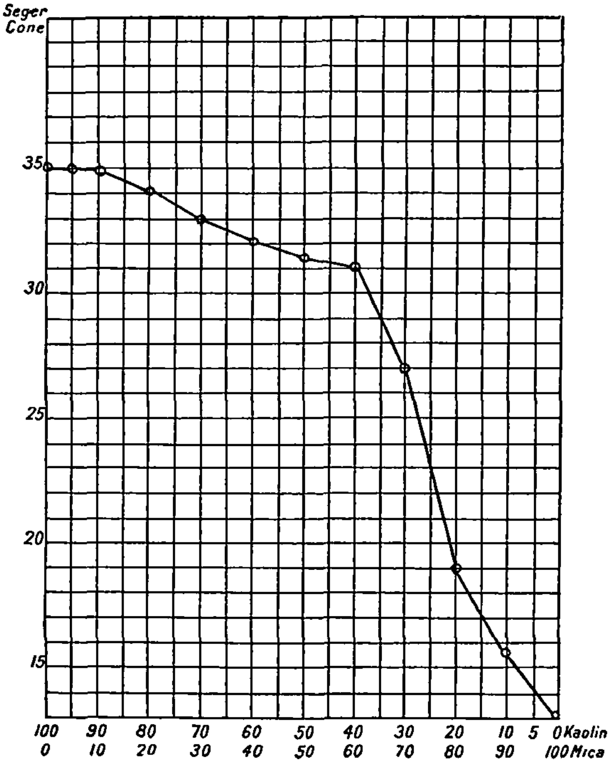

FIG. 3.—Refractoriness of mixtures of kaolin and mica.

As already noted, *felspar* is sometimes an impurity in china clay and kaolin ; its effect is readily understood from a study of the melting-points of a series of mixtures of felspar and clay containing each substance in known proportions. Similarly, the addition of mica or of other substances to a pure clay and an examination of the properties of the mixture gives an excellent idea of the effect of these substances when present as impurities.

The effect of the addition of felspar and quartz to a pure clay is shown in Table II., which is due to Simonis.[2]

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[1] See Tables III., IV., and XXIX.

[2] *Sprechsaal*, 1907, Nos. 29, 30.

TABLE II.—EFFECT OF HEAT ON MIXTURES OF KAOLIN, QUARTZ, AND FELSPAR.

No.	Zettlitz Kaolin.	Quartz.	Felspar.	Fusing-Point (Seger Cone).
1	..	15	85	9–10
2	..	30	70	14
3	..	45	55	15–16
4	..	55	45	17
5	..	70	30	26–27
6	..	85	15	30–31
7	15	..	85	–9
8	15	15	70	10–11
9	15	30	55	13–14
10	15	45	40	15
11	15	55	30	17–18
12	15	70	15	–26
13	15	85	..	28–29
14	30	..	70	14
15	30	15	55	16–17
16	30	30	40	17–18
17	30	45	25	–26
18	30	55	15	26
19	30	70	..	27
20	45	..	55	26+
21	45	15	40	26–27
22	45	30	25	27–28
23	45	45	10	29
24	45	55	..	29–30
25	55	..	45	28
26	55	15	30	29–30
27	55	30	15	30+
28	55	45	..	30–31
29	70	..	30	31+
30	70	15	15	32
31	70	30	..	32+
32	85	..	15	33–34
33	85	15	..	33–34

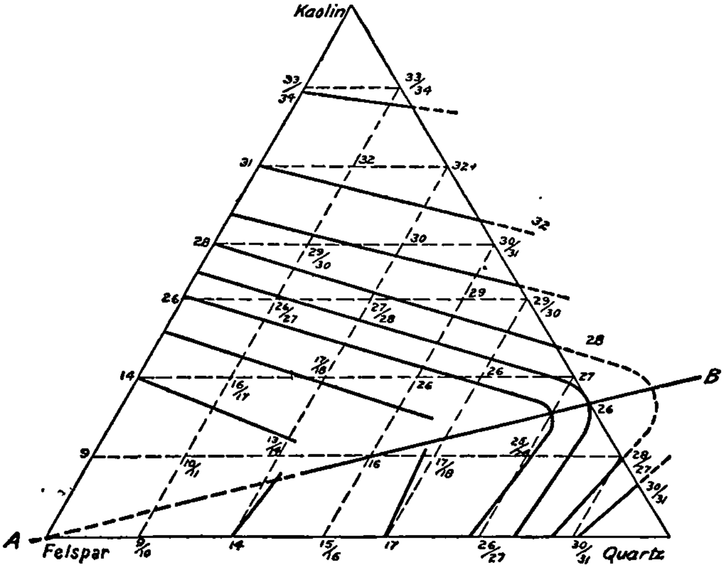

Fig. 3A.—Refractoriness of felspar, quartz, and kaolin mixtures.

Purdy has represented part of Table II. in the form of a triaxial diagram (fig. 3A), in which the darker parallel lines are those of equi-refractoriness. The line A B may be termed an *eutectic axis* ; it is drawn from the clay-quartz eutectic to the felspar apex. The numbers are those of the Seger cones which " bend " at the same temperatures as the mixtures. The shapes and directions of the equi-refractory curves seem to show the existence of two fluxes: (*a*) felspar, (*b*) a clay-quartz eutectic; no felspar-quartz eutectic is shown in this figure.

The effect of felspar is discussed further on p. 88, as it is an important impurity in some clays. Its precise effect is peculiarly difficult to determine, because the term " felspar " is applied not merely to one chemical compound but to a group of such compounds of similar chemical constitution but differing widely in their composition. Thus, orthoclase or potash felspar behaves quite differently from anorthite or lime felspar, and albite or soda felspar behaves differently from either. It is, therefore, of the greatest importance, in carrying out investigations of this character, to ascertain accurately which kind of felspar is present.

The sizes of the various particles used also affects the nature of the compound formed, because the amount of combination which occurs is largely dependent on the duration of the heating and on the closeness of the contact of the various reacting particles. If the heating is sufficiently prolonged, the same eutectic will be formed no matter what proportions are used in the mixture, but with insufficient heating an entirely different eutectic may be formed.

Flach has studied the effect of various metallic oxides on the refractoriness of Zettlitz kaolin (taken as typical of a pure clay), with the results shown in the two following tables[1]:—

TABLE III.—EFFECT OF HEAT ON MIXTURES OF KAOLIN AND QUARTZ.

No.	Zettlitz Kaolin. Per cent.	Quartz. Per cent.	Molecular Formula.	Percentage Composition.					
				With 5 per cent. Fluxes.		With 10 per cent. Fluxes.		With 15 per cent. Fluxes.	
				Zettlitz Kaolin. Per cent.	Quartz. Per cent.	Zettlitz Kaolin. Per cent.	Quartz. Per cent.	Zettlitz Kaolin. Per cent.	Quartz. Per cent.
a	15	85	0·106RO . $1Al_2O_3$. 28·1SiO_2	14·25	80·75	13·50	76·50	12·75	72·25
b	17	83	0·102RO . $1Al_2O_3$. 24·6SiO_2	16·15	78·85	15·30	74·70	14·45	70·55
c	19	81	0·099RO . $1Al_2O_3$. 21·8SiO_2	18·05	76·95	17·10	72·90	16·15	68·85
d	21	79	0·096RO . $1Al_2O_3$. 19·5SiO_2	19·95	75·05	18·90	71·10	17·85	67·15
e	23	77	0·094RO . $1Al_2O_3$. 17·4SiO_2	21·85	73·15	20·70	69·30	19·55	65·45
f	25	75	0·092RO . $1Al_2O_3$. 15·8SiO_2	23·75	71·25	22·50	67·50	21·25	63·75
g	27	73	0·090RO . $1Al_2O_3$. 14·4SiO_2	25·65	69·35	24·30	65·70	22·95	62·05
h	29	71	0·089RO . $1Al_2O_3$ 13·3SiO_3	27·55	67·45	26·10	63·90	24·65	60·35
i	31	69	0·088RO . $1Al_2O_3$. 14·4SiO_2	29·45	65·55	27·90	62·10	26·15	58·65
k	33	67	0·087RO . $1Al_2O_3$. 11·5SiO_2	31·35	63·65	29·70	60·30	28·05	56·95
l	35	65	0·086RO . $1Al_2O_3$. 10·6SiO_2	33·25	61·75	31·50	58·50	29·75	55·25
m	38·25	61·75	0·085RO . $1Al_2O_3$. 9·6SiO_2	36·34	58·66	34·43	55·57	32·51	52·49
n	41·22	58·78	0 084RO . $1Al_2O_3$. 8·6SiO_2	39·16	55·84	37·10	52·90	35·03	49·97
o	44·19	55·81	0·083RO . $1Al_2O_3$. 7·9SiO_2	41·98	53·02	39·71	50·23	37·56	47·44
p	47·16	52·84	0·082RO . $1Al_2O_3$. 7·3SiO_2	44·80	50·20	42·44	47·56	40·08	44·92
q	50·13	49·87	0·081RO . $1Al_2O_3$. 6·7SiO_2	47·62	47·38	45·12	44·88	42·61	42·39
r	53·10	46·9	0·081RO . $1Al_2O_3$. 6·2SiO_2	50·45	44·55	47·79	42·21	45·14	38·86
s	56·07	43·93	0·080RO . $1Al_2O_3$. 5·7SiO_2	53·27	41·73	50·46	39·54	47·66	27·34
t	59·04	40·96	0·080RO . $1Al_2O_3$. 5·3SiO_2	56·10	38·90	53·14	36·86	50·18	34·82
u	62·01	37·99	0·079RO . $1Al_2O_3$. 4·9SiO_2	58·91	36·09	55·81	34·19	52·71	32·29
v	65	35	0·079RO . $1Al_2O_3$. 4·6SiO_2	61·75	33·25	58·50	31·50	55·25	29·75

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[1] *Sprechsaal*, 1911, Nos. 12–15.

TABLE IV.—EFFECT OF HEAT ON MIXTURES OF KAOLIN AND FLUXES.

No.	Fusing Point.[1]	$CaCO_3$.		$SrCO_3$.		$BaCO_3$.		$MgCO_3$.		Na_2CO_3		K_2CO_3.		$KNaCO_3$.	
		5 per cent.	10 per cent.	10 per cent.	15 per cent.	10 per cent.	15 per cent.	5 per cent.	10 per cent.	5 per cent.	10 per cent.	5 per cent.	10 per cent.	5 per cent.	10 per cent.
a	32	28	+26	+27	−26	+27	+26	27	27	+27	+20	+28	26	27	26
b	31	+27	26	27	20	+27	26	26	−27	27	+20	+28	−26	−27	−26
c	+30	+27	20	−27	−20	27	−26	−26	+26	+26	+20	28	−26	−27	−26
d	29	+26	20	26	19	−27	−26	+20	26	+26	20	−28	−26	26	20
e	+28	26	+19	−26	−19	−27	20	20	+20	26	−20	−28	20	−26	−20
f	28	26	19	+20	+18	+26	−20	+19	20	−26	−20	−28	20	−26	19
g	−28	19	18	20	18	26	+19	19	19	−26	−19	−27	−20	−26	18
h	+27	18	+17	19	+17	−26	+19	+18	17	−20	−18	−27	19	20	18
i	27	17	17	−19	17	−26	+19	18	+16	19	16	20	−19	20	−18
k	28	17	+16	18	+16	20	+18	+17	+16	+19	17	26	−19	−20	−18
l	+28	+17	16	−18	15	−20	18	17	16	20	+17	+26	18	−20	18
m	29	+17	+15	−17	−15	+19	17	+17	+15	+20	+17	+26	+18	+19	−19
n	+29	+17	14	+16	14	+19	16	+17	+15	+20	18	+26	+19	+19	−19
o	−30	+17	+13	+16	+13	20	17	−18	15	26	+18	+26	20	+20	19
p	30	19	+13	+16	+13	+20	+17	18	14	27	19	27	+20	+26	+19
q	+30	20	−13	+17	13	26	18	19	14	28	+19	+27	26	27	+19
r	−31	+20	13	+17	+13	+26	+18	+19	+15	+28	20	+27	+26	28	+20
s	31	26	14	18	−14	+26	+18	20	+15	+28	+20	28	+27	+28	+20
t	+31	+26	14	19	+14	27	19	+20	+15	29	+20	+28	+27	29	+20
u	−32	+26	+15	+19	+15	+27	+19	26	+15	+29	26	29	28	+29	26
v	32	+26	16	20	+16	+27	+19	+26	16	+29	+26	+29	+28	+29	+26

The effect of mica on the refractoriness of kaolin has been found by Rieke[2] to be as follows :—

TABLE V.—EFFECT OF HEAT ON MIXTURES OF KAOLIN AND MICA.

Composition of Mixture.	Fusing-Point (Seger Cones).	Composition of Mixture.	Fusing-Point (Seger Cones).
100 Zettlitz kaolin,	35	50 Zettlitz kaolin, 50 potash mica	31–32
95 „ „ 5 potash mica	35	40 „ „ 60 „ „	31
90 „ „ 10 „ „	35	30 „ „ 70 „ „	27
80 „ „ 20 „ „	34	20 „ „ 80 „ „	19
70 „ „ 30 „ „	33	10 „ „ 90 „ „	15–16
60 „ „ 40 „ „	32	— „ „ 100 „ „	13

The same results are shown graphically in fig. 3. It is interesting to compare them with those which Rieke obtained with mixtures of mica with pure alumina (Table VI. and fig. 4) and pure silica (Table VII. and fig. 5) respectively (see also *Mica*, p. 90).

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[1] Fusing-point of the quartz-kaolin mixture *without* any added fluxes.
[2] *Sprechsaal*, 1908, No. 42.

TABLE VI.—EFFECT OF HEAT ON MIXTURES OF MICA AND ALUMINA.

Composition of Mixture.	Fusing-Point (Seger Cones).	Composition of Mixture.	Fusing-Point (Seger Cones).
100 mica,	13	70 mica, 30 alumina	17
90 „ 10 alumina	12	60 „ 40 „	30
80 „ 20 „	13	50 „ 50 „	36

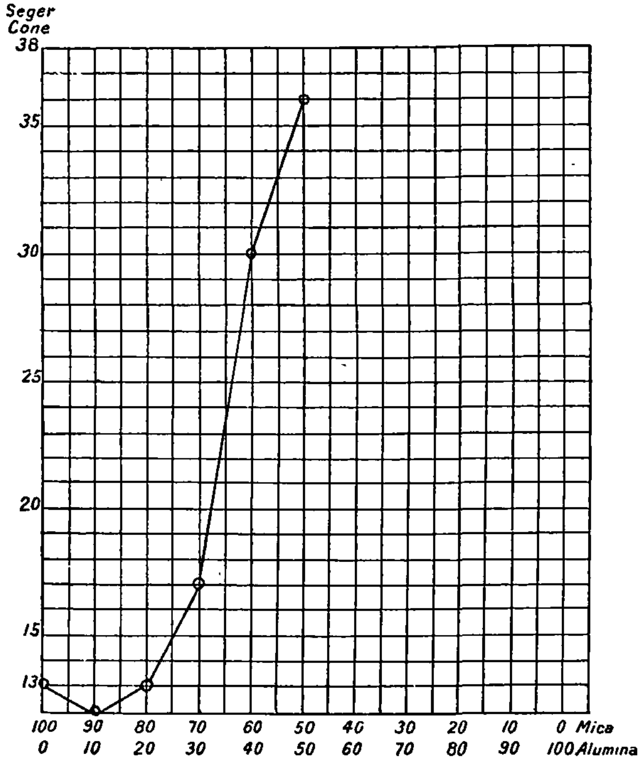

FIG. 4.—Refractoriness of mixtures of mica and alumina.

TABLE VII.—EFFECT OF HEAT ON MIXTURES OF QUARTZ AND MICA.

Composition of Mixture.	Fusing-Point (Seger Cones).	Fusing-Point of the previously fused Mixture (Seger Cones).	Composition of Mixture.	Fusing-Point (Seger Cones).	Fusing-Point of the previously fused Mixture (Seger Cones).
100 quartz,	36	36	40 quartz, 60 potash mica	20	14–15
90 „ 10 potash mica	32	31–32	30 „ 70 „ „	20–26	15
80 „ 20 „ „	28	26–27	20 „ 80 „ „	27	18–19
70 „ 30 „ „	20	19–20	10 „ 90 „ „	14	6–7
60 „ 40 „ „	20	17	— „ 100 „ „	13	7
50 „ 50 „ „	18	14			

The lower fusion-point of some previously fused mixtures of silica and mica suggests the formation of a definite compound on prolonged heating.

The effect of the addition of silica to kaolin is shown in Table XLIII.

Binding Clays.—There are several important refractory materials which are devoid of plasticity, and cannot be made into bricks, etc., without some binding agent. For some of these materials the most satisfactory bond is a highly plastic clay. Hence, binding clays[1] play an important part in the manufacture of refractory goods. They are so plastic that they enable a quantity of non-plastic or less plastic material to be mixed with them to form a single mass of such plasticity and mechanical strength as will make a useful product. They are chiefly used to bind together the refractory grog or the lean clays used for the manufacture of refractory blocks, bricks, crucibles, etc.

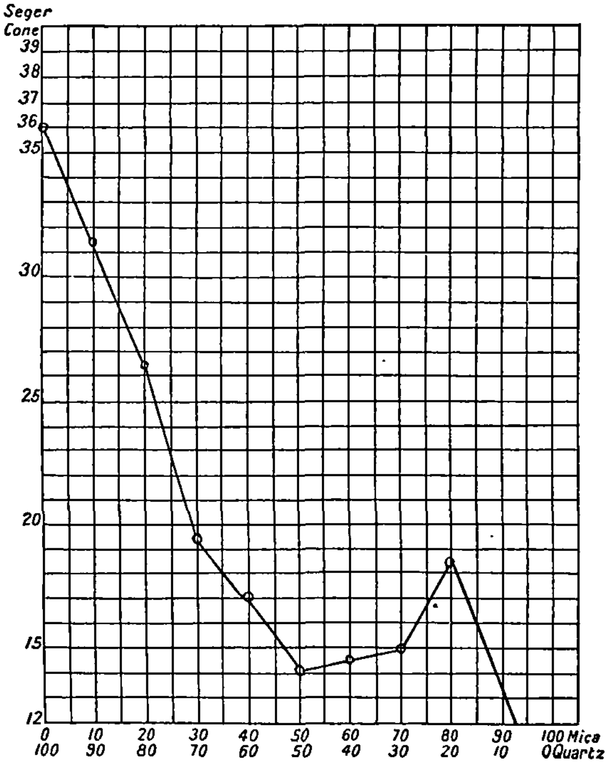

FIG. 5.—Refractoriness of previously fused mixtures of mica and quartz.

In Great Britain, firebricks and other refractory articles are chiefly made from raw fireclay, but in Germany a superior article is obtained by the use of non-plastic grog or "burned clay" and a plastic binding clay of the ball-clay

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[1] Care must be taken not to confuse binding clays with *binds*, which are quite different. "White bind" and "grey bind" indicate shales of the colour named, whilst "stony bind" is a sandy shale, and some structureless clays are known as "soft binds," the terms really referring to layers or strata of material, just as miners use the term "seam" to mean a layer or stratum of coal. A "bind" is not a binding clay and need not be plastic.

type. Ball clays which are not sufficiently pure to be used for white ware, but are otherwise of high quality, are, in fact, representative of the best binding clays.

A good binding clay will not only enable a lean clay or grog to be worked readily, but will give to the mixture containing it a greater strength, both before and after burning, than it would otherwise possess. Some binding clays only possess one of these characteristics, and, whilst facilitating the shaping of goods made of lean material, produce, on burning, so brittle and tender a product as to be practically useless. On the other hand, some china clays have but little influence on the plasticity of the mass, yet greatly increase the strength of the burned product.

Binding clays are usually fat, plastic clays, which cannot be used alone for the manufacture of refractory goods; but simple inspection will not indicate whether a clay is a good binding clay. The only way of ascertaining this is to make trials with various proportions of grog, and then to make porosity, tensile, and " fusion " tests on these mixtures. For a binding clay to be satisfactory it must be highly plastic, and neither too refractory nor so fusible as seriously to lower the heat-resistance of the mass of which it forms a part (see " Binding Power ").

The most important binding clays in Great Britain are the ball clays, but some of the more plastic fireclays, notably in the south of Yorkshire, the north of Derbyshire, and in parts of Warwickshire and Staffordshire, also possess great binding power. Their refractoriness is well over Seger Cone 26, and their great strength when fired more than makes up for their somewhat low heat resistance.

If a certain proportion of one or two of these clays be added to the main clay above mentioned, it will confer on the latter a far greater power of resistance to the pressure of the surrounding brickwork or of the contents of the furnace, as the case may be.

The binding power of a clay may usually be increased by purifying the material and especially by suspending it in water with the aid of little alkali, running the suspension, or slip, from the coarser impurities, and then either precipitating the suspended matter by adding a little acid, by evaporating off the water, or separating the clay by an electric current. There is, however, a marked limit to the increase in binding power which can be obtained with any given clay; it appears to be limited to the removal of impurities rather than to any notable increase in the true binding power. When plastic clays are stored in the form of a paste, a slight increase in binding power is usually noticeable.

Ball Clays.—Some of the ball clays of Dorset and Devonshire are sufficiently resistant to heat to be classed as refractory clays, but their importance in the manufacture of refractory goods lies less in their intrinsic resistance to heat than in their great plasticity and binding power. They are able to unite or bind a considerable quantity of non-plastic material or slightly plastic clay, forming a mass of sufficient plasticity to be easily worked, and in this way they are extremely valuable in the manufacture of goods from materials which do not of themselves possess sufficient plasticity. The use of highly plastic clays is essentially one of compromise, the manufacturer being compelled to forgo a slight reduction in the heat-resisting power of his most refractory material in order that he may produce goods of great strength and highly resistant to corrosion by slags, abrasion, etc., and to impart the necessary toughness, adhesion, and plasticity to the body mixture, only sufficient being added to produce these effects, and an excess being avoided on account of its deleterious effect on the refractoriness of the whole.

The refractory ball clays in Devonshire are chiefly of Tertiary origin ; in North Wales and Derbyshire there are considerable deposits of both black and white ball clays which are distinctly different from those of Dorset and Devonshire.

The principal deposits of Devonshire ball clays are found round Kingsteignton, Teingrace, Homers, Decoy, and Newton Abbot in South Devonshire, and near Mariond and Merton (Torrington) in North Devonshire. The ball clays obtained from South Devonshire are all comprised within the Bovey basin, which is a depression about 10 miles long by 2½ miles wide, and extending from Bovey Tracey to about 2 miles south of Kingskerwell—watered by the Teign and the Bovey which have their sources in the granite rocks of Dartmoor. The clay contains fragments of iron pyrites varying in size from a small shot to that of a hen's egg. Water-worn stones of quartz and slate also occur, together with detached pieces of lignite. The beds in North Devonshire (especially in the Torrington district) are similar to those in the south, and extend for a distance of about 20 miles towards Dartmoor, though the workings are chiefly at the northern end of the basin.

The principal deposits in Dorsetshire are in the district known as the Isle of Purbeck, where the river Frome and its tributary stream, Poole Harbour, and the English Channel practically enclose Hamworthy, Wareham, Goathorn, Corfe Castle, and Swanage. The "Purbeck" ball clays resemble the Devonshire ones, but are less refractory. They occur in alternation with beds of pale yellow or buff-coloured siliceous sands and loams and beds of flint pebbles, whilst beneath the clay is a seam of earthy brown coal somewhat similar to the lignite found beneath the beds in South Devonshire at Bovey. Limestone and marl beds, chalk, with or without flints, and beds of varicoloured clays also occur. The so-called " ivory " ball clays (which burn to a creamy colour) occur in extensive deposits associated with more or less sandy clays, loams, and gravel beds to the north of the river Frome and round Poole, Parkstone, and Bournemouth. The Devonshire ball clays are usually slightly lower in iron than those of Dorset, but the difference in colour of the fired ware made from each is not great. These ball clays are generally considered to have been produced from china clay in the Dartmoor district and to have gained their plasticity by frequent transportation from there to their present position. G. Maw and others consider, however, that the ball clays are not derived from the Dartmoor granites, but from the Chalk to which they are in close proximity, the chalk itself having been removed from them by the action of carbonated water.

The conversion of china clay into ball clay (if it ever occurs) is a process which appears to require several hundred years. The precise nature of the conversion is not known ; what appears to be the most probable explanation suggests that the clay has been subjected to a powerful grinding action in the presence of very faintly alkaline water, whereby the clay particles were converted into extraordinarily minute colloidal particles. These particles were subsequently coagulated by contact with water rendered faintly acid by decomposed vegetable matter, the coagulum being deposited and afterwards rendered compact by the pressure of the overlying deposits. Unfortunately, the necessary conditions do not appear to be producible by artificial means, so that the production of ball clays has never been successfully imitated artificially.

Ball clays are frequently quarried in open workings, but sometimes the overburden of soil, sand, and other useless material is so great that mining is preferred. In some cases, even when the overburden is very great, it pays to remove it with a steam navvy so as to obtain greater accessibility to the ball clay, the cost of removal being less than that of mining and timbering. This is particularly the case where old pits are being re-worked.

The clay, which occurs as a stiff, plastic mass, very difficult to dig, is cut into rectangular or cubic blocks or " balls " weighing about 36 lbs. each, and measuring about 9 inches by 6 inches by 5 inches. It is from these that ball clays derive their names. The men work in three sets, one cutting lengthwise (" long scoring "), another cutting at right angles (" thwarting "), and the third (" diggers ") following and cutting at a depth of about 8 inches with a wide heavy tool, kept lubricated by frequently dipping its blade into water. These " balls," selected according to quality, are raised to the surface by hand or steam power, and are then taken to the stores by sliding them down a shallow trough or toboggan, or by means of tipping-wagons hauled mechanically.

The practice, adopted in coal mines, of a central shaft with many horizontal headings is seldom adopted in mining ball clays ; the commoner practice is to sink a fresh shaft as soon as the distance to which the clay has to be carried underground becomes inconveniently great.

After mining, the clay must be stored in heaps to weather, or in warm cellars, some clays being improved and others damaged by frost. It is important that the heaps should not be placed near hedges or trees, and before being " heaped " the clay balls must be pared and scraped. The alleged inferiority of modern ball clays is sometimes attributed to the employment of youths for this clay-paring instead of the much older and more careful men who did it in past years. During the formation of the heap, the clays are blended or mixed, some firms priding themselves on the skill of their workmen in this connection.

In Devonshire, the thickness of clay is so great that the bottom has not yet been reached in some districts, but in Dorset it is more usual to find deposits of 15 or 20 feet, or even less. In some parts, the total depth of clay is far greater, but much of it is too impure for use in refractory work. In Devonshire, distinction is made between " White," " Tough," and " Auzey " or " Rose " ball clays, and between other ball clays stained by organic matter and other impurities, including the pink, blue, dark, and sandy yellow clays. At Wareham, where the best Dorset ball clays are obtained, mining is necessary. At Messrs Pike Brothers' " Furzey Ground," for example, the shaft is about 120 feet deep, and the " cuttings "—which are generally about 5 feet high—extend beneath a large pool of water of considerable depth ; consequently, the mining operations are attended with great difficulty. The clay, on being extracted from the mine, is conveyed further down the sidings to the " heaps," where it is " weathered " for at least two years, being turned over periodically to admit of better seasoning and to ensure evenness throughout.

Some of the better qualities are also obtained by carefully washing the clay and passing it through a No. 200 sieve and then into settling ponds before shipment.

The stoneware ball clays, which occur nearer the surface, are worked by open quarrying. They are usually too fusible to be used for refractory work.

In *chemical composition*, the ball clays do not differ greatly from the china clays, except that they often contain a rather larger proportion of alkalies and iron, are more vitreous when fired, but do not burn so white as the china clays. When freshly dug, they contain upwards of 30 per cent. of water, of which about 20 per cent. is removed on drying at 100° C., but the remainder only at a dull red heat. As ball clays are usually stored in open sheds, the quantity of water will vary much, according as the season is summer or winter. The difference between the ball clays and china clays is much more in their relative plasticity than in chemical composition.

A typical ball clay suitable for increasing the plasticity of a refractory material will show on analysis—

Silica	40 to 48 per cent.
Alumina	32 to 36 „
Iron oxide	less than 2 per cent.
Lime and magnesia	„ 1 „
Potash and soda	„ 3 „

The upper beds of the clay frequently contain a considerable amount of sand, and the best quality is only found at a considerable depth. The latter is unctuous and is free from sand and grit.

Before firing, ball clays are dark-coloured—sometimes approaching black—owing to the organic matter they contain, which probably has some connection with their extraordinary degree of plasticity. Ball clays often contain 3 or 4 per cent., or even a larger proportion, of carbon in the form of lignite or other organic matter, chiefly of vegetable origin, though this is seldom reported separately in analyses, being included in "Loss on Ignition."

The best selected varieties of Devonshire ball clays are perfectly black, with a bright, glossy appearance, and no ordinary observer would suppose that they will burn to a white body.

The *colour* of ball clays in their natural raw state has no connection with their colour after firing, as the blue (or black) coloration from which the clay derives its name is chiefly due to carbonaceous matter which burns away entirely in the kiln, leaving a white or very creamy-white mass. Ball clays (either raw or burned) are never quite so white as china clays. The purest varieties, when burned, are almost white, but others are stained by carbonaceous and other materials. The material sold as "white clay" varies in tint from snow white to a pale straw colour, and still lower qualities gradually shade off into yellow and khaki colours. The ball clay which, when burned, yields "pink clay" also occurs, usually in patches, in the white-burning clays; the pink coloration is probably due to ferric oxide or other iron compounds, though the small proportion of iron shown on analysis makes this doubtful. The suggestion that the pink colour in some raw clays is due to vegetable matter is more feasible, though as these do not all contain vegetable matter, the colour may be of mineral origin.

The *plasticity* and *binding power* of ball clays are extremely high, but do not admit of accurate measurement owing to the complexity of the forces which combine to produce the plastic state. Various ball clays may be compared by mixing different quantities with a definite amount of flint or grog and water and ascertaining which ball clay will bind the largest quantity of non-plastic material into a plastic mass. In effecting this comparison, some attention should be paid to the shrinkage of the test pieces, as some ball clays shrink excessively when dried. Any ball clay which, if made into a tile 6 inches in length, shrinks more than ¾ inch when dried, should be discarded as soon as an equally plastic clay with less shrinkage can be obtained. In making this tile, nothing but water should be added to the clay.

The *texture* of ball clays is difficult to describe, on account of the great plasticity of the material. The grains are so surrounded by water as to have the appearance of a jelly, but if the texture is destroyed by rubbing the clay gently with water, a slurry containing extremely fine particles of clay is produced. The grains are somewhat coarser than those of china clay, but the best samples of ball clay, when made into a slip with water, will pass entirely through a sieve with 100 meshes per linear inch. Such a slip shows colloidal characteristics similar to those of a china clay slip made in a similar manner.

When *heated*, the more refractory ball clays decompose at a temperature near 500° C., with loss of water; at a rather higher temperature any organic matter present burns away, and at a bright red heat a porous whitish mass is obtained. If the temperature is raised still higher, vitrification commences, the pores being gradually filled with fusible matter which, on cooling, binds them into a hard glassy mass of great strength and toughness. Notwithstanding the production of a large amount of this fused material, the best ball clays do not lose their shape until heated to a temperature corresponding to Seger Cone 32 or just above. This combination of vitrifiability without loss of shape is of great value in the use of ball clays as binders in the manufacture of refractory goods. The heating curve of ball clays is similar to that obtained on heating china clay (fig. 2). According to Hodsman and Cobb, ball clay has a mean expansion from 0° C. to 1000° C. of 0·57 per cent.

The *impurities* in ball clays are chiefly (*a*) *carbonaceous* matter, which burns away in the kiln and is, therefore, unimportant when they are used for refractory work; (*b*) *pyrite* and *mundic*, two forms of iron sulphide, which form black slag-like masses in the burned clays and tend to increase their fusibility: both mundic and pyrite should, therefore, be removed by picking or washing whenever practicable; (*c*) *free silica*; (*d*) various silicates, of which *mica* is the most typical,[1] and several iron, lime, and magnesia compounds.

Further information on ball clays will be found in *Special Reports of the Mineral Resources of Great Britain*, **31**, by A. Scott (H.M. Stationery Office).

FIRECLAYS.

The term "fireclay" is commonly applied to the more refractory clays occurring in the geological formations known as the Coal Measures, though it is also used for any refractory clay.[2]

Using the term in its conventional sense as excluding the kaolins and ball clays described in the foregoing pages, fireclays may be regarded as those which will not show signs of loss of shape by partial fusion when heated to 1580° C. in a clean oxidising atmosphere, the temperature having risen steadily from 15° C. at the rate of 10° C. per minute.

The best-known deposits of fireclay in the United Kingdom[3] are the Upper and Middle Coal Measures of the Carboniferous Series—the Lower ones consisting of siliceous rocks.

Table VIII. shows the various strata in which fireclays occur in their geological order.

The refractory clays of the Coal Measures are of two types: (1) shales, and (2) underclays.

The *shales* constitute the bulk of the deposit, but are seldom as refractory as the underclays. Indeed, they are often so siliceous as scarcely to deserve the name of clays. They are essentially siliceous clays which have been

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[1] The "alkalies"—potash and soda—in ball clays are usually present in the form of fusible silicates, but soluble alkali-salts are sometimes present.

[2] Some geologists regard all clays found immediately beneath a coal seam as fireclays; but this use of the term is undesirable, and unless such clays are known definitely to be refractory, they are better described as *underclays*.

[3] Many of the Continental and American fireclays do not correspond in appearance and qualities with British grey Coal Measure fireclays, but more closely resemble our ball clays and china clays. Of these foreign clays, the *flint clays* are the most important; they are described later.

TABLE VIII.—GEOLOGICAL DISTRIBUTION OF FIRECLAYS.

System.	Group.	Localities.
Post-Tertiary	Pocket-clays	Derbyshire, Staffordshire, N. Wales.
Tertiary	Pleistocene	..
	Pliocene	..
	Miocene	..
	Oligocene	Devonshire basin deposits.
	Eocene	Woolwich and Reading beds, Surrey.
Cretaceous	Chalk	..
	Greensand	..
	Wealden	Fairlight clays, Sussex.
Oolite (Jurassic)	Oolite (upper)	..
	Oolite (middle)	..
	Oolite (lower)	Upper Estuarine series.
	Lias	..
Permian	..	..
Carboniferous	Upper Coal Measures	Lancashire, Warwickshire, N. Staffordshire.
	Middle Coal Measures	Cumberland, Lancashire, Cheshire, Northumberland, Durham, Leicestershire, N. Staffordshire, S. Staffordshire, Shropshire, Warwickshire, N. Wales.
	Lower Coal Measures	Lancashire, Durham, Northumberland, Yorkshire, N. Staffordshire, N. and S. Wales, Central valley of Scotland, Ayrshire.
	Millstone grit	Lancashire, Cheshire, Forest of Dean, Central valley of Scotland, Ayrshire, Fifeshire.
	Carboniferous limestone	Renfrewshire.
Devonian	..	Ayrshire.
Silurian	..	..
Ordovician	..	Shropshire.
Cambrian	..	Warwickshire, Worcestershire.
Pre-Cambrian	..	Anglesey, Argyllshire, W. Inverness-shire.
Metamorphic	..	..
Igneous	..	Decomposed granite in Cornwall and Devonshire.

laminated by bedding. Their normal colour is grey, but on the outcrops they are often brown or yellow, due to oxidation of the contained iron salts. Unlike the underclays, these shales have been deposited in definite layers; they are apparently derived from sources quite different from the underclays.[1]

Underclays, also known as *seat-earth*, *spavin*, and *warrant*, lie immediately beneath the coal seams. They vary greatly in composition, from an aluminous clay to a siliceous rock (ganister), and are generally thought to be the old soils in which grew the plants which later formed the coal seams, or else a marine-estuarine ooze which has been repeatedly shifted and re-sorted. From these ancient soils the alkalies have been removed by the growth of vegetation. In no place is the evidence more clearly visible than in the Yorkshire Coalfield, in which, on descending through the Measures, fireclay or ganister is found beneath one seam of coal after another with the utmost

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[1] *Slates* are metamorphosed shales; they are not suitable for the manufacture of refractory materials on account of their lamellar nature. Notwithstanding this fact, several patents for the use of a mixture of slate débris and fireclay or silica have been granted, notably those to H. H. Hickman in 1880, and to J. Davies in 1891.

regularity.[1] Moreover, in these underclays it is quite usual to find masses of clay filled with fossilised remains of the roots of sigillaria and the leaves of other plants.

Some authorities contend that true fireclays originated from the oxidation of the lower part (or, in some cases, the whole) of the coal seam, basing their argument on the fact that coal-ash appears to consist very largely of calcined clay, and on the fact that if the underclays were soils, the lower parts of the bed ought to be richest in lime and other bases and gradually rise to purer clays, but they do not. Further, the coal seams are often too thin to make it reasonable to suppose that they purified so great a thickness of soil as the underclay beneath.

The underclays, which constitute the best fireclays, generally consist of soft, greyish clay of moderate plasticity which crumbles more or less readily when weathered; it usually has a soapy feel, has curved lines of fracture, and does not always split in planes parallel to the bedding, though some beds are slightly stratified. The beds are usually horizontal, though some have a pronounced inclination or dip. The composition of a bed varies greatly in different areas in the same locality, and even in samples taken one below another at the same part of the bed. Hence, it is not wise to assume that all the clay under a given seam of coal is of the same value, for that is seldom the case. The variation in a vertical direction is best observed by means of a microscope, which will show the different proportions of crystalline matter (usually felspar and sand with some mica) and clay. Thus, in fig. 7, the "mild" clay, rich in alumina, predominates at the top of the seam, gradually changing to the "strong" or siliceous clay at the bottom, with the "medium" clay containing the well-known Stourbridge "Pot" clay between.

The Coal Measure clays are chiefly worked in Staffordshire, Warwickshire, Shropshire, Yorkshire, Northumberland, Durham, Derbyshire, Leicestershire, Nottinghamshire, West Scotland, and Wales, though fireclays occur beneath the coal seams in each of the other coalfields (see *Frontispiece*).

Thus, in addition to the well-known fireclay deposits mentioned above, the underclays of the Coal Measures in Gloucestershire, Somerset, Kent, and Wales yield excellent fireclays, but so far they have not been well developed industrially. To some extent this is due to the better known fireclays being so situated that their owners can deal adequately with all the ordinary demands of the market, and to the majority of firebrick manufacturers and colliery owners failing to realise the advantages of systematically purifying their clays and then catering for more than a local trade. There are great possibilities in such a policy, particularly in Wales.

The Yorkshire, Derbyshire, and Notts fireclays are comprised in the coalfield of that name, within an area obtained by drawing straight lines between Wilsden or Bingley, Halifax, Huddersfield, Penistone, Ambergate, Stapleford in Notts, Shireoaks, Pontefract, Church Garforth, and Baildon near Bradford. It is, however, extremely probable that the eastern boundary of this area should be extended into Lincolnshire, where it is buried beneath Permian and Triassic rocks (see dotted areas in *Frontispiece*).

In **Yorkshire** there are about seventy fireclay mines; they yield the following useful fireclays:—

1. Better Bed fireclay.

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[1] Clays of precisely the same properties as underclays sometimes occur apart from any coal seam. They appear to have been produced in the same manner as the underclays, but no coal-producing plants have grown over them. In the following pages no distinction is made between these clays and the underclays which they so closely resemble.

2. Hard Bed Band fireclay or White Car clay.
3. Thirty-six yard fireclay.
4. Halifax Hard Mine fireclay.
5. Halifax Soft Bed fireclay.
6. Pot clay.

The relative positions of the various Yorkshire beds will be seen from the diagram below.

Superficial beds.
Fireclay.
Gritstone.
Shale.
Whinmore and Penistone coals.
Drain-pipe clays (Penistone).
Gritstone and shales.
Better Bed coal.
Better Bed fireclay (Leeds).
Elland flagstones.
Shales.
Halifax Hard Bed coal.
Ganister.
Halifax Hard Bed fireclay.
Shale.
Bind (firestone).
Bastard ganister.
Fireclay.
Shale.
Middle Band or Clay coal.
Fireclay.
Middle Rock and Firestone.
Shale.
Halifax Soft Bed or Coking coal.
Halifax Soft Bed fireclay.
Crawshaw flagstones.
Shale.
Thin coal.
Sheffield-Huddersfield fireclays and Pot clay.
Bind.
Millstone Grit.

The Yorkshire fireclays are of widely varying composition, the alumina content ranging from about 12 per cent. to over 30 per cent.

In the Leeds district the "Better Bed underclays" take the highest rank, the underclays of the Black Bed, which is nearer the surface, being of inferior fireclay.

What is commonly known as the "Leeds Bed" occurs near the town of that name, and covers an area of about thirty square miles. It is generally understood that the other fireclays in this district are suitable for refractory goods of medium quality, but not for making the most refractory articles, glazed bricks, and other accurately shaped ware, for which the true "Leeds" clay is specially valuable on account of its low proportion of organic and iron compounds. The "Leeds" clay occurs in two seams—one relatively near the surface, and the other nearly seventy fathoms below; the upper portion of the deep one is the most valuable part of the deposit. It occurs immediately beneath the "Better Bed" coal. The clay found nearer the surface is usually tender, more plastic, and shrinks more than the deep-mine clay. This is objectionable for glazed goods and for large pieces of refractory ware, but less so for firebricks, particularly if ground burned firebricks or "grog" be added. This "tender" clay is slightly richer in alumina than the strong clay found below it, and indicates a material somewhat richer in true clay.

Leeds fireclay is not rich in alumina, and corresponds in chemical composition to a mixture of equal parts of pure clay (alumino-silicic acid) and free silica, with a tendency to contain more free silica; some seams are more aluminous.

The "*White Car*" *clay* lies below the Halifax Hard Bed Band coal, some distance below the Better Bed coal. It is worked at Shipley, Elland, Siddal, Deighton, and Deepcar; near Huddersfield it is used, together with silica rock, as a material for sagger manufacture. At Hipperholme, near Halifax, the "White Car" clay bed is about 10 feet thick, and is strong and aluminous. It has a rather larger proportion of iron compounds and a much lower content of alkalies, so that it is one of the most refractory clays on the Yorkshire coalfield. In the Don valley, it occurs near Deepcar in a bed which is less rich in alumina than that near Huddersfield, and, owing to its low proportion of alkalies, it is of value for refractory articles which are required to retain their shape accurately at a high temperature. The " White Car " clay has a low shrinkage, and when completely vitrified it has a high resistance to acids, and so is useful for chemical stoneware. The bed of " White Car " clay is of limited extent and, unfortunately, it is not uniform in character. The southern portion of it is used for drain-pipes and other forms of common stoneware, but the north-western portion contains so large a proportion of pyritic nodules as to be almost useless.

The 36-*yard fireclay* is extensively used round Halifax for refractory bricks, gas retorts, acid-resisting goods, and sanitary ware. At Elland, the bed of clay is 6 feet to 7 feet thick.

The "*Halifax Bed*" consists of two distinct series of seams, and also extends over a large area. The upper series—known as the " ganister " or " Hard Mine coal "—consists of hard coal underlain by ganister and fireclay, and below it, separated by a great thickness of sandstones and siliceous shales, is the " Soft coal " or " Low Bed." The ganister is made into silica bricks and tamped furnace linings, and the " Hard Mine fireclay," immediately beneath it, is manufactured into similar articles to those made from the "Leeds Bed" clays. Most of the works making refractory goods from the upper Halifax fireclay are situate at Elland and near Halifax, as further north and east it gradually alters and comes nearer to the surface, but is then very suitable for the manufacture of salt-glazed and engobed goods. To the south-east it is much used for drain-pipes and for a moderate quality of firebricks, but is very liable to be contaminated with iron ore, which occurs in thin veins in it.

In the district having Elland as a centre, the proportions of the different strata vary greatly, and in some parts of this area ganister occurs in place of the " shale and inferior clay " shown in fig. 6.

In composition, the Halifax fireclay is somewhat siliceous, the best specimens corresponding to Stourbridge " deep mine " or to a mixture of true clay (of same composition as kaolin) with rather more than an equal weight of free silica,[1] but some portions of the bed are of distinctly inferior quality.

The *Halifax Soft Bed underclay* near Sheffield is moderately plastic, and may be used as a binding clay, but it is too siliceous and contains too much iron and alkali to make firebricks of the best quality. To the north-west of Sheffield it is richer in alumina and somewhat more refractory.

The " *Stannington Pot clay*," or " *Stannington black fireclay*," occurs near the base of the Lower Coal Measures, about 10 feet above the Rough Rock or Millstone Grit. It has long been valued for the manufacture of crucibles used in steel-melting. The intervening beds consist of sandy bind and mudstones. Some parts of the bed are 10 feet thick. At Loxley, the working thickness is 7 to 8 feet at the outcrop, tapering to 5 feet in the direction of the dip of the strata. The best qualities occur near the outcrop, where the clay is extremely refractory and sufficiently plastic for all ordinary purposes; further in the clay is more stained, less refractory, and much less plastic, the difference being attributed to the clay nearer the outcrop having been subjected to the prolonged action of water percolating through the fissures in the bed, so that the soluble impurities have largely been washed out. A much more important reason for the popularity of the pot clay lies

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[1] This way of expressing the composition of a clay is more convenient than accurate, as explained on pp. 6 and 70.

in the fact that the clay near the outcrop has taken up water and is swollen considerably, so that its plasticity is well developed. Further away from the outcrop the clay is inferior in quality, and 200 yards or more from the surface it is of little value, being then usually too rich in carbonaceous matter, iron compounds, and alkalies, which cause the clay to "bloat" when heated.

The best qualities of Stannington Pot clay contain about 39 per cent. of alumina, which is a larger proportion than in most fireclays.

A bed of fireclay which is regarded as equivalent to the Pot clay underlies a considerable area of the Coal Measures of the Yorkshire and Nottinghamshire coalfield, and reaches from Leeds almost to Nottingham; on the outcrop, it is highly refractory.

Seams of so-called "fireclay" occur in Yorkshire in association with almost every seam of coal, but, except for those mentioned above, they are too thin to be worked profitably, or are so impure as to be insufficiently refractory. When abundant, the latter are used, as at Penistone and Denby Dale, for making building bricks, tiles, and drain-pipes.

A refractory clay from the Lower Oolite formation in Commondale, Yorkshire, is made into firebricks and domestic fireblocks.

In **Northumberland** and **Durham** there are a very large number of fireclay mines—about 35 in Northumberland, and 65 in Durham. Most of the clays are used for the production of sanitary ware and for firebricks of No. 2 grade. Some of the Weardale fireclays are more refractory than those of the Tyneside.

The diagram on p. 50 gives, in descending order, the more refractory fireclays actually used.

The position of the following Coal Measure fireclays—all of which are used—has not been identified by the Geological Survey:—Queen, Wonder, Plessy, Beaumont, Engine, Townley, and Barlow.

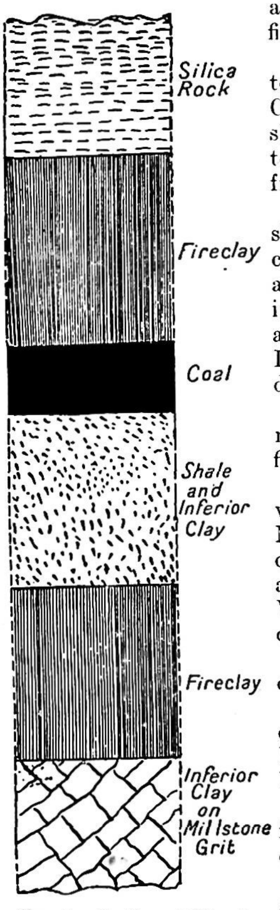

FIG. 6.—Section at Elland, Yorks.

The *Stone Coal fireclay* has been largely worked in the Blaydon district; it contains about 72 per cent. of silica and 25 per cent. of alumina. The *Yard Seam fireclay* is rather richer in alumina and poorer in silica, whilst the *Five Quarter Seam fireclay*, which is worked in the north-west of Durham, sometimes contains 30 per cent. of alumina and 63 per cent. of silica.

The *Lister Seam fireclay* at Scotswood-on-Tyne is of excellent quality, and has long been used for the manufacture of glazed sanitary ware as well as firebricks.

The *Busty Seam fireclay* is about 3 feet thick; it occurs at a depth of about 450 feet between two beds of Busty Seam coal. It is worked near Brancepeth and Tudhoe, where it is mixed with the clay from the Brockwell

Seam, which occurs at a lower level. The Busty clay is devoid of stratification, is of good quality, and contains, on an average, about 66 per cent. of silica and 22 per cent. of alumina, thus corresponding very closely with some of the Stourbridge fireclays.

The *Brockwell Seam fireclay* is the most important in the district and is worked over an area of about 160 square miles. It varies in thickness from 1 foot 6 inches to 2 feet 6 inches, contains about 30 per cent. of alumina, and is usually of excellent quality. This clay, together with that from the Busty Seam, is chiefly used for coke-oven bricks and semi-ganister bricks. A seam worked in the Witton district called the *Marshall Green Seam* is also used for ganister bricks.

Fireclay beds also occur in the Carboniferous Limestone Series of Northumberland and Durham, though they are not so well marked or so important as those above. One of the best of these beds of fireclay occurs at South Tyne Colliery, about 240 feet above the Little Limestone coal. It consists of 2 feet 6 inches of good coal and 3 feet of a clay of second-class quality.

Near Corbridge is a 5–6 feet seam which occurs beneath the Blue Limestone. This clay is contaminated in places with spar and nodules of iron pyrites, but selected portions are useful for the manufacture of drain-pipes, and semi-vitrified goods.

Other fireclays of varying thicknesses and quality occur at Dipton, Heydon Bridge, and New Ridley.

Hutchings has made a remarkable statement (*Geol. Mag.*, 1890, p. 271) that the Northumbrian fireclays consist of a mixture of mica, quartz, and felspar, with only a small proportion of material too minute for identification. Such a statement is

Middle Coal Measures.

Stone coal.
Fireclay.
Measures.
Yard coal.
Fireclay.
Lister coal.
Fireclay.
Measures.
Main coal.
Measures.
Bensham or Maudlin coal.
Fireclay.
Measures.
Low Main coal.
Measures.
Hutton coal.
Fireclay.
Measures.
Bottom Harvey, Tilley or Constantine coal.
Constantine fireclay.
Measures.
Top Busty or Ballarat coal.
Ballarat fireclay.
Measures.
Five Quarter or Bottom Busty coal.
Fireclay.
Measures.
Busty or Three Quarter Busty coal.
Busty fireclay.
Measures.
Top Brockwell or Top Main coal.
Fireclay.
Measures.
Brockwell, Bottom Brockwell, or Main coal.

Lower Coal Measures.

Fireclay.
Measures.
Victoria coal.
Fireclay (Witton ?).
Measures.
Marshall Green coal.
Fireclay.
Measures.
Tow Law ganister.
Fireclay.
Measures.

Millstone Grit—No refractory clays.

Carboniferous Limestone.

Shales, sandstones.
Fell Top limestone.
Shales, sandstones.
Limestone.
Corbridge fireclay.
Shales, sandstones with limestones.
Fireclay (Haltwhistle).

inconsistent with the known properties of these clays, and cannot be accepted without further proof as to its accuracy.

"Post clay" is a local name for a highly siliceous fireclay which is generally useless.

The **Cumberland fireclays** extend from the south of Whitehaven to Wigton, and lie chiefly along the coast and under the sea. They are much cut up by faults. There is a probable extension of the clays under the Permian rocks both north and south of the exposed Coal Measures.

The most useful fireclays occur in association with the Fireclay Band coal at Seaton Moor, Moorhouse Guards, and St Helens, the Bannock Band coal at Whitehaven and Oatlands, the fireclay or Ganister Seam at Gillhead and Camerton, and the Forty-three Yard coal at Micklam, Wythemoor, and Branthwaite.

In some of the Cumberland works, a felspathic grit known as *Barfs stone* is used instead of grog.

The **Lancashire** fireclays may be regarded as similar to the Yorkshire ones. They occur in a triangular area extending from Colne to Huyton on the south-west and to Stockport on the south-east, with a narrower area extending to Macclesfield and east to Chapel-en-le-Frith. Between Bury and Blackburn, however, there is an area of fifty square miles of Millstone Grit quite devoid of coal. This area is much intersected by faults, and working is made difficult by the steep inclination of the deposits. In the Blackburn-Burnley area (which includes the well-known works at Accrington, Darwen, and Littleborough) the most useful fireclay is the underclay of the Mountain Mine or Ganister coal, which appears to correspond to the Halifax Hard Bed coal, though the underlying ganister is more aluminous than the Yorkshire ganister. The underclays of the Cannel, Upper Mountain Mine, and Inch Mine coals are also used.

In the Wigan, Horwich, and St Helens area, the most useful fireclays are the underclays of the Upper, Middle, and Lower Mountain Mine coals, the Middle Mountain Mine clay being the best. The Yard Mine, Wigan Four-foot, Trencherbone, and Ganister fireclays are also used near Wigan, and the Pigeonhouse, Park Mine, and Arley Mine clays near St Helens.

In South-east Lancashire and East Cheshire, the most useful fireclays are underclays of the Four-foot coal in the Middle Coal Measures, the White Ash or Half-yard fireclay near Stockport, the Ganister or Lower Mountain Mine fireclay near Macclesfield, Oldham, and Doffcocker near Bolton, the Lower Foot Mine fireclay at Thurston Clough, Delph near Oldham, and Jericho near Bury, and the No. 2 fireclay at Thurston Clough in the Lower Coal Measures, and the Victoria fireclay at Grolton near Oldham, in the Millstone Grit. Of these, the Ganister or Lower Mountain Mine fireclay is one of the most frequently used.

On the left bank of the river Dee—from Mostyn to Hawarden and thence south to Oswestry—is an important Coal Measure area with several outliers on its north-western extremity, Wrexham being the most important town in this district—to the clayworker.

The **Midland** fireclays extend over a very wide area, comprising the coalfields of Staffordshire, Leicestershire, Warwickshire, Shropshire, and Gloucestershire.

In **Staffordshire** and **Warwickshire** the fireclays crop out, and are known (erroneously) as marls, but the best qualities occur at a considerable depth, and probably extend westward and southward under the Permian and Triassic rocks. The "saggers" used in the Staffordshire potteries are chiefly made from these local fireclays, but the most famous fireclays are found in the Dudley coalfield in the neighbourhood of Stourbridge, where the material is largely used for the manufacture of retorts, firebricks, blocks, and other refractory goods.

The **North Staffordshire** or Potteries coalfield extends from Congleton to Longton and almost to Stone, its western extremity being Madeley, and its eastern one Oakmoor. Clays occur in the Keele Beds, Newcastle sandstone, Etruria marls, and the Black Band series. Of these, the most useful fireclays are the so-called " cane marls " below the Bassey Mine, Littlerow and Peacock coals.

The Etruria marl series, which are 800 to 1000 feet thick, lie immediately below the Newcastle shales, which are 300 to 500 feet thick, but are of much less importance, and in turn lie above the Black Band series from which the coal is obtained. There are, however, many strata which are not refractory, and are useless for purposes for which highly refractory clays are required. They are really fireclays and are not true marls,[1] as the percentage of lime compounds is trifling. Each bed has its own peculiar characteristics. These " marls " are worked at Tunstall, Cobridge, Hanley, and Fenton in North Staffordshire, and in various parts of South Staffordshire.[2] Saggers are also made from the Great Row marl, Cannel Row, Chalky Mine, Knowles, Rusty Mine, and Ash marls. Other fireclays are associated with the Half-yard Ironstone, Burnwood, Single Four-foot, Rough Seven-foot, Birches, Holly Lane, Eight-foot, Banbury, Winney, Penny, and Bee coals.

The North Staffordshire area is rich in clays, but the deposits are irregular, often steeply inclined, and sometimes almost vertical. The South Staffordshire deposits are more regular, but are cut by igneous dykes.

The South Staffordshire coalfield extends due south from Armitage to Walsall, and thence to Halesowen, with Wolverhampton just beyond its western boundary, and Stourbridge just outside its south-western one. In this area the Grey Measures are overlain by the Permian rocks, the Halesowen sandstone, and the Old Hill marls.

The *Stourbridge fireclays* are by far the best known in South Staffordshire, " Stourbridge firebricks " having been manufactured since 1780 or possibly earlier, and at the present time there are about forty firebrick works in this area. The fireclay varies very considerably in composition, according to the particular stratum from which it is obtained, and much now being placed on the market is not superior to that from other districts. The best Stourbridge clay is characterised by its high alumina, plasticity, refractoriness, and low kiln shrinkage. This last is about half that of the Northumbrian, Yorkshire, and Scotch fireclays, and seldom exceeds 3 per cent. The strata near Stourbridge are much faulted, and the fireclay has been upheaved so as to be available in many places when only shallow shafts are used. These higher deposits are rapidly being worked out, and the lower portions of strata are coming more into use.

The principal mines from which Stourbridge clays are obtained are situated between two faults, the Western Boundary Fault and Hayes Fault, *i.e.* in an area bounded by Stourbridge, Naggersfield, and Kingswinford on the west, and by Homers Hill and Saltwells on the east.

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[1] A true marl is a mixture of calcium carbonate (" chalk ") and clay. The term " sagger marl " is largely used for fireclays of the Middle and Upper Coal Measures of Staffordshire, which are sufficiently refractory to be used in the production of saggers, bats, tile-boxes, quarries, etc., used in potters' kilns ; the similar materials in other parts of the country being termed " fireclay " or " bind."

[2] An instructive description of these strata is given in the Memoir on *The Geology of the Country around Stoke-on-Trent,* published by the Geological Survey.

The most important fireclay seams in this district are the " Old Mine " seam, and the " New Mine " seam which lies below it. As they are not associated with coal, their correlation with clays in various parts of the area is very difficult, but the officers of the Geological Survey have reached the conclusion that the following order (as shown in the diagram) is reasonably correct, but tentative :—

Brooch coal.
Thick coal.
Upper Heathen coal.
Four-foot earth.
Lower Heathen coal.
Bottom rock.
(Sulphur coal).
Broad earth.
Old Mine clay.
(New Mine coal).
No. 1 New Mine clay.
(Fireclay coal).
No. 2 New Mine clay.
(Bottom coal).
No. 3 New Mine clay.
No. 4 New Mine clay.
No. 5 New Mine clay.
Other New Mine clays.

The *Old Mine seam* occurs in two areas separated by the Netherton Anticline—

(*a*) The Brettell Lane, Delph, Amblecote, and Lye area ; and

(*b*) the Cradley area.

The vertical position of the beds varies, but is usually 4 to 16 yards below the thick coal seam.

In the Brettell Lane area the Old Mine clay varies from 3 to 7 feet in thickness; near Cradley, it seldom exceeds 3 feet in thickness, and is overlain in parts by a Sulphur or Stinking coal. To the west of Brettell Lane, it is bounded by the Western Fault, and in a north-westerly direction, towards Dudley, the underclay of the Sulphur coal has different properties from those of the Old Mine clay.

Whilst the Old Mine clay varies considerably in different places, it may usually be divided into three parts—

(*a*) An upper, almost black, mild clay containing 40 per cent. of alumina.

(*b*) A central stronger clay containing 25 to 28 per cent. of alumina, and including the well-known Stourbridge Pot clay.

(*c*) A lower strong clay containing 25 per cent. of alumina.

Great care has to be observed in getting it, as, if the miners are careless, too much material is " blown up," and the lower seam, containing impurities (locally known as " cannucks " or " iron nodules "), becomes mixed with the clay.

The *New Mine fireclay* occurs in five seams from 3 to 6 feet thick over practically the whole of the coalfield at a distance of 9 to 13 yards below the Old Mine coal. Fig. 7 shows a section at Naggersfield where only two seams of New Mine fireclay are recognised, but to the south-east, in the Bowens and Delph No. 3 pits, three and four seams occur respectively, whilst at Rufford and John Hall No. 2 pits there are five seams. The beds are underlain by binds, sandstone, and marls; in some parts of the Stourbridge area, they are overlain by several other beds of fireclay of varying thickness. In some localities to the north of Naggersfield, there are eight fireclay beds beneath the No. 1 New Mine fireclay.

The No. 1 New Mine clay is the best known, and is 4 to 5 feet thick. Unfortunately, it is liable to sudden changes in texture and character. Nos. 2 to 5 are usually inferior in quality to the No. 1 clay.

The clays from the New Mine beds are increasingly used as the Old Mine clays are worked out, and, notwithstanding the fact that the former are nearly always less refractory than the latter, they are sold without discrimination as " Best Stourbridge Fireclay " !

There are also several inferior fireclays which occur above the Main Coal of the Stourbridge area, but they can only be used for unimportant work. Some of the beds, which are commonly termed fireclays, are not sufficiently refractory to deserve the name, though they might be termed " bastard fireclays." They occur chiefly in the marl beds, and contain 54 to 70 per cent. of silica, 15 to 16 per cent. of alumina, 1 to 3 per cent. of alkalies, and 1½ to 11 per cent. of iron expressed as ferric oxide. Their colour varies from dull red to greenish-yellow or ashy colour, the green being due to the presence of chlorite and epidote as impurities. These beds are chiefly used for the manufacture of "blue bricks" and floor tiles, but some of the buff-burning portions are used for firebricks which are required to be of great mechanical strength rather than resistant to high temperatures.

In winning the clay, care has to be taken to avoid mixing the products from distinct seams; for, although seams occur in close proximity to one another, their chemical constituents and properties are by no means similar. Thus, a highly desirable substance may be found side by side with one containing an abnormal proportion of deleterious salts.

Under the microscope the "strong" clay shows many well-defined crystalline particles; the "medium" clay has a few such crystals in a mass of amorphous material; and the "mild" clay appears to consist entirely of amorphous matter. The "mild" clays are more plastic, and are considered to make stronger and tougher bricks than the "strong" ones.

In **Warwickshire**, the fireclays are chiefly used for glazed bricks and chemical stoneware, as they vitrify somewhat readily. In East Warwickshire, the Grey Measures are overlain by the Lower Permian rocks, the Haunchwood sandstone, and Nuneaton clays. The Nuneaton fireclay is exceptionally suitable for glazed brick manufacture; it probably extends under the Permian rocks into the South Staffordshire coalfield.

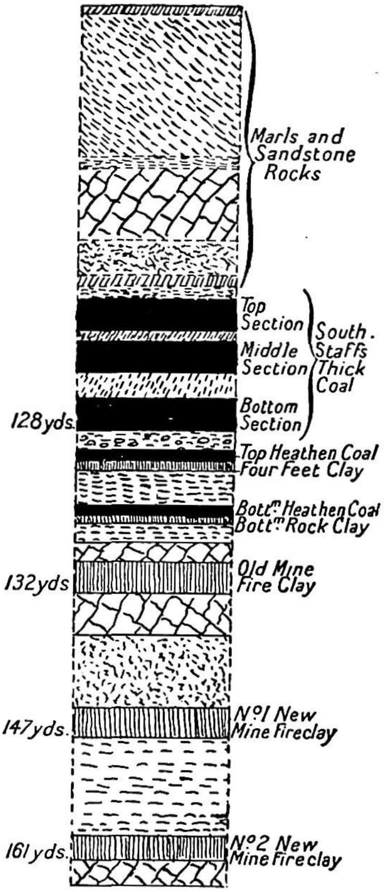

Fig. 7.—Section at Naggersfield, near Stourbridge.

The **Leicestershire** and **Derbyshire**[1] area contains a group of fireclays near the top of the Middle Coal Measures, which corresponds with a similar group of clays in North Staffordshire (Black Band clays) and Flintshire (Buckley clays). In Derbyshire and Leicestershire these clays are in two distinct groups: (*a*) near Swadlincote, Church Gresley, Woodville, and Moira, and (*b*) east of the Erewash Valley; these eastern clays have scarcely been worked.

The Leicestershire and Derbyshire fireclays are rather less refractory than those of Stourbridge, on account of the presence of nearly 4 per cent. of lime, magnesia, potash, and soda.

Of these various fireclays, the only one of importance is known variously as

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[1] The highly siliceous fireclays found in "pockets" in Derbyshire are described later.

the "Fireclay Seam," "Main Fireclay" or "Derby Clay," which is a fat grey fireclay having a thickness of 3 to 12 feet. This clay crops out on the north-west near Church Gresley, but its north-eastern and southern boundaries have not been clearly defined. Formerly the clay was largely used in the manufacture of steel, but since the introduction of electric furnaces the chief uses of the *Leicestershire* fireclays have been for salt-glazed sanitary ware, domestic fireplaces, etc.

The whole of the Trent district above the Midland coalfields may be regarded as a possible site for fireclay works, and the Nottinghamshire collieries are, in several cases, utilising their fireclay advantageously for pipe-making and for No. 2 firebricks, though the fireclays in Nottinghamshire are only of moderate refractoriness and are not really suitable for the manufacture of refractory goods.

The "Sida" clay, obtained from beneath the ganister near Chesterfield, is a well-known refractory clay, though richer in iron than the best fireclays.

In **Lincolnshire,** especially at Stamford and in the surrounding district, fireclays are worked along with an outcrop of the Upper Estuarine series which lies below the Great Oolite and rests on the Lincolnshire Oolite limestone. There are two "fireclays," locally known as "Skerry" and "Grey Clay" respectively. Considerable quantities of fireclay from other localities are mixed with these clays before they are used.

The **Shropshire coalfield** extends from Dorrington, almost due south to Bewdley and Stockton in Worcestershire, but it may also lie under Triassic rocks on its northern and eastern boundaries. In the Coalbrookdale area are several fireclays below the Pennystone Ironstone in the Middle Coal Measures, some parts of these clays being highly aluminous, but their correlation is by no means complete. The two most important fireclays in this area are the Horsehay New Mine clay and the Ladywood Ganey clay.

The principal mines in this district are near Broseley, Jackfield, and Coalport. The most refractory clay lies immediately below the Ganey coal, in a stratum about 2 feet thick. It contains nodules of ferrous carbonate, but after weathering burns to a pale cream colour.

In **Worcestershire,** the best Bewdley fireclays from Wyre Forest are used locally in the Worcester potteries. They resemble the fireclays of Stourbridge, but are richer in iron oxide, and are somewhat less refractory.

In **Gloucestershire** and **Somerset,** there are two coalfields, one covering the greater part of the Forest of Dean, and the other extending from Wickwar to rather south of Bristol, with three small areas to the south at Chew Magna and Poulton, and a probable extension of indefinite area under the Triassic and Liassic rocks in Somerset.

The Coal Measure clays of Somerset and Gloucestershire have not been used at all extensively, in spite of their suitability for firebricks of fair quality, and the fact that they are sufficiently rich in bituminous matter to be cheaply burned. This is partly due to the deposits being so thin in places as to be unprofitable. In the *Forest of Dean coalfield,* there is only one firm engaged in the manufacture of refractory goods, and these are made of a highly siliceous clay at the top of the Millstone Grit.

In **Cornwall** and **Devonshire,** there are no true fireclays, but firebricks are made of (i) the decomposed granite which is the source of china clay, and consists of a heterogeneous mixture of china clay, quartz, mica, and partially decomposed felspar; (ii) the waste residues from the china clay works, and especially those known as "micas," which contain some china clay irregularly distributed amongst much mica, quartz, and finely divided felspar; (iii) inferior china and ball clays deposited in pockets along with felspar, etc. The impurities contained in them prevent them from being highly refractory—though pockets of exceptionally refractory material are occasionally found.

Some of the firebricks made of these materials are regularly used for lining furnaces and are quite satisfactory.

The Oligocene ball and stoneware clays of Devonshire occurring in the Bovey Basin, which extends in a north-westerly direction from Newton Abbot, and in the Torrington Basin n North Devon, are used for the manufacture of firebricks, but the more plastic portions are chiefly of value as binding agents.

The **Kent** coalfield is wholly concealed, and has a partially proved area of about 200 square miles. The northern boundary lies north of the river Stour, but for the most part south of the northern coastline of Kent. The southern boundary lies far out to sea beneath the English Channel, but has not been located. The Coal Measures consist of the Transition series (1700 feet to 2000 feet thick), and the Middle Coal Measures (2000 feet thick). The Lower Coal Measures and the Millstone Grit are unrepresented. This coalfield is supposed to be one of a series of detached coal-basins which extend from Somerset and Gloucestershire in a due easterly direction and are connected to the Belgian coalfields.

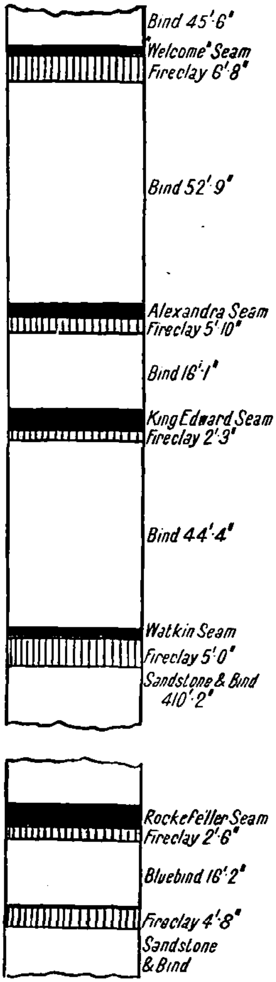

Fig. 8.—Section at Waldershare, Kent.

Chalk	813 ft.
Gault	163 „
Lower Greensand	70 „
Wealden	42 „
Oolite	301 „
Lias	5 „
Coarse sandstone and shales	376 „
Hard grey bind	45 „
Welcome seam	2 „
Fireclay	6 „
Grey bind	53 „
Alexandra seam	3 „
Fireclay	6 „
Grey bind	16 „
King Edward seam	4 „
Fireclay	2 „
Grey bind	44 „
Watkin seam	1 „
Fireclay	5 „
Sandstone and bind	410 „
Rockefeller seam	5 „
Fireclay	2 „
Blue bind	16 „
Fireclay under 4 in. coal	5 „
Sandstone and bind	155 „

The fireclays in the Kentish coalfield have not been fully examined, partly because some preliminary tests were disappointing. They showed that the Kentish fireclays resembled those in South Wales. The beds at Waldershare are shown in the above section and in fig. 8. At Stonehall and Goodnestone the coal seams are more numerous, but not all have fireclays beneath them.

It will be seen that the Coal Measures lie at a depth of some 1400 feet below the surface, and no useful fireclay occurs at a less depth than 1818 feet, where the " Welcome Seam " consisting of about 6 feet 8 inches of moderately good fireclay is found.

In the *London Basin, i.e.* between the Chilterns and the North Downs, there are no Coal Measure clays, but a loamy sand which occurs in the Woolwich and Reading beds at Esher, Ewell, and Epsom is known as a " fireclay." It is much used in the South of England, though bricks made from it are red and would not, ordinarily, be recognised as firebricks. These bricks contain nearly 5 per cent. of ferric oxide, but this does not prevent their satisfactory use in gas-works.

Firebricks of fair quality were formerly made at Hedgerley, near Windsor, from *Windsor loam.*

In **Scotland,** the fireclays are chiefly worked in Lanarkshire, Dumbartonshire, and Stirlingshire, especially at Cadder, Gartcraig, Cardowan, Garnkirk, Heathfield, Glenboig,[1] Castlecary, Bonnybridge, Kilmarnock, Gartcosh, Glasgow, Kirkcaldy, Alloa, etc.

Fireclays of good quality occur in other parts of Scotland, but they are usually less refractory than those found in the localities just mentioned, and only serve the more local markets.

The Scotch fireclays occur in four geological horizons: (i) the Lower Coal Measures, (ii) the Millstone Grit, (iii) the Carboniferous Limestone, and (iv) the Calciferous Sandstone. Their position is shown on p. 58.

The Coal Measure fireclays chiefly underlie coal seams and are true underclays, but they are rarely of great refractoriness, though extensively used for various purposes. Thus, several collieries near Newmains, in Lanarkshire, mine a fairly hard greyish fireclay with a very low shrinkage which is used for refractory goods and furnace linings. In the Shettleston district, a fireclay of fair quality is mined for firebrick manufacture, and in Linlithgowshire and Stirlingshire there are several thick beds of fireclay of good quality occurring immediately beneath the workable coal seams, which are used for the manufacture of refractory goods, including stove backs, etc. Near Kilmarnock, the Coal Measure fireclays are worked on a large scale, particularly those associated with the Turf, Ladyha, Wee, Darrock, and Stone coals. Of these, some of the Wee coal fireclay is perhaps the best quality. The principal articles made are sanitary ware and second-class firebricks. At Falkirk, a fireclay overlying the Slatyband Ironstone and a ganister clay associated with the Bonnyhill Craw coal are used.

The principal seams of coal and fireclay in Scotland occur below the Millstone Grit, instead of above it, as in other localities. Although the detached areas comprising this coalfield may to some extent account for this observation, it is equally possible to regard it as a confirmation of an essential difference in

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[1] *Halloysite* is said to occur in Glenboig fireclay, but J. W. Mellor has found no trustworthy evidence of such occurrence. Halloysite may occur in very small quantities in other fireclays and china clays, and to a limited extent as a natural earth, though seldom, if at all, in Great Britain. Its composition is very variable, but usually contains from 39 to 45 per cent. silica, 20 to 40 per cent. alumina, and 10 to 26 per cent. water. When heated at 150° C., a variable proportion (3 to 12 per cent.) of water is given off, and, according to Zirkel, at 250° C. kaolinite is formed ; but Mellor states that free alumina, silica, and water are produced. The crystals are soft, somewhat soapy in appearance, generally opaque, but transparent at the edges, and become more transparent when in water. Their colour varies from bluish white to green or grey. According to Ries, halloysite is never crystalline, the crystalline form being *pholerite.* Halloysite is most frequently found as rough nodules with a conchoidal fracture, harder than talc, but softer than gypsum, and with a specific gravity of 1·9 to 2·1. It is moderately plastic. (See also Howe (*op. cit.*), pp. 158 and 252.)

nature which has been observed in the Scotch fireclays from Glenboig and those from other localities.

The best Scotch fireclays are unusually refractory, and as bricks and other articles made from them are burned at a much higher temperature than is usual in England, they have gained a great reputation for non-shrinkage when used in furnaces, though the shrinkage in the kiln is often very great.

Kiltongue coal.
Fireclay.
Strata.
Upper Drumgray coal.
Strata.
Lower Drumgray coal.
Fireclay.
Strata.
Smithy coal.
Strata.
Gas coal.
Strata.
Mill coal.
Strata.
Ball coal.
Fireclay.
Strata.
Fireclay.
Main coal.
Fireclay.
Strata.
Colinburn coal.
Fireclay.
Strata.
Bonnyhill Craw coal.
Fireclay.
Strata.
Fireclay.
Slatyband Ironstone.
Strata.
Upper fireclay.
Strata.
Fireclay.
Strata.
" Silica Rock " and fireclay.
Strata.
Fireclay.
Strata.
Fireclay.
Strata.
Fireclay (Blue seam) }
Silica rock } *Lower fireclay.*
Fireclay (Main seam) }
Strata.
Curdly Ironstone.
Cement Limestone.
Cement fireclay.
Strata.
Fireclay (White seam).
Castlecary Limestone.

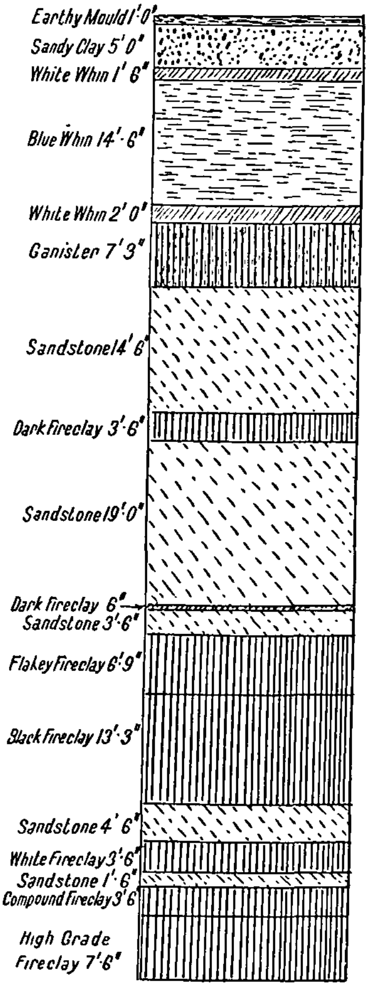

FIG. 9.—Glenboig fireclay seam.

In the Glenboig district, which includes the greater part of the country between Garnkirk and Glenboig, there are two principal seams of fireclay, one being at the top and the other at the bottom of the Millstone Grit series.

In the Lower fireclay series, the best portion of the clay at Glenboig is that which lies above the Main clay, and is known at the Gain Workings as the " Blue Clay." The chief seam (fig. 9) crops out at Old Works and lies at a distance of only 12 to 30 feet above the limestone, but is worked at a depth of 500 feet at Star Works, the dip being very rapid. The seam used is the lowest of several, the others being of less value. It varies in thickness from 2 inches to 3 feet; its composition also varies, some parts of the bed containing a large proportion of iron; but it is of such a nodular nature that much of it can be removed by picking; the remainder appears to do little or no harm. Some parts of the clay are fossiliferous, marine shells occurring in large quantities; these portions are, of course, useless as a refractory material. In some parts of the Glenboig district, the Lower clay occurs in two beds, the chief one being 6 to 12 feet thick, but reduced in places to a thin band of no commercial importance. The variable thickness and false bedding of the Glenboig clays suggest that they have been deposited as fine siliceous sediments which were afterwards greatly eroded by currents of water.

In comparison with the amount available, the fireclays of the Glenboig district have only been exploited to a comparatively small extent, and a very considerable area remains to be developed.

The Gartcosh clays are rather less refractory than those at Glenboig, and in the Linlithgowshire, the uppermost grey clay is the most refractory and the one most generally suitable for firebricks.

In the east and south of the coalfield, the Lower fireclay occurs in beds of varying thickness, reaching 10 feet between Torphichen and Levenseat. In Ayrshire, the Lower fireclay is known as the Monkcastle clay; it lies below 36 to 240 feet of lava-flows, interbedded with foul coals, fireclays, and ganisters. It is extremely irregular in thickness, varying from 20 feet to a few inches, and in some places being wholly absent. On the northern side of Fenwick-water, near Kilmarnock, a 7-foot seam occurs which is very low in alkalies, and at Kilwinning the same bed splits into four parts, and has a total thickness of 10 feet. Its plasticity is very low; its refractoriness corresponds to Cones 33 to 35. In Southern Ayrshire, the Lower fireclay lies about 60 feet above the bottom of the Millstone Grit, and is mixed in conjunction with ironstone, which occurs 150 feet above it at Dalmellington and Cumnock. It is of excellent quality, and is used for making refractory bricks and blocks for furnace work.

The Upper fireclay at the top of the Millstone Grit occurs at Bonnybridge, Torbanehill, and Hareshaw, and consists of several seams varying from 2 to 8 feet in thickness, the whole being included in a total working thickness of about 22 feet, including a bed of coal 3 inches to 2 feet in thickness.

It is interesting to compare fig. 9 with the strata worked at Bonnybridge, which is only a few miles from Glenboig. The Bonnybridge strata are—

Sandstone.
Top fireclay (4 to 5 feet thick).
Coal.
Brown stone.
Ganister.
Fireclay (5 to 7 feet thick).
Inferior ganister (1½ feet thick).
Sandstone.

The clay is very irregular in composition, and some of the beds are occasionally missing, especially towards the north. The top fireclay is overlain by a useful silica rock. The beds occupy a considerable area, and have been identified on the eastern side of the coalfield near Allanton and Salsburgh and also at Torphichen. Ironstone nodules occur in the Upper fireclays, and clay ironstone in the Hareshaw beds.

The " Ayrshire Bauxitic Fireclay " occupies a position corresponding to the Upper fireclay (which latter does not appear in Northern Ayrshire) at the top of the Millstone Grit series. This bauxitic fireclay is a grey, moderately hard, aluminous rock which breaks into rough cubes with a conchoidal fracture; it is quite devoid of plasticity. The proportion of bauxite present (as judged from solubility in acid) must be quite small, being usually 4 to 10 per cent., the total alumina content being about 39 per cent. This clay contains a relatively large proportion of iron and titanium oxides and other adventitious minerals. The clay varies in refractoriness from Cones 29–37. The most refractory clay has an oolitic appearance. It is used for highly refractory ware, but is not of great value where a dense body is required. When making into articles, it must be mixed with a binding clay, Newcastle, Yorkshire, and ball clays being used for this purpose. The area occupied by the bauxitic clay has not been fully defined; it appears to extend from South Bay, Saltcoats to Kilwinning, east to Lugton Water and south to Annick Water. Further outliers occur to the north at Lockwood and Smithstone and to the south at Kirkconnel, and it may occupy much of the area between Dalry and Dalmellington, as well as part of the Isle of Arran.

These bauxitic clays have not been fully exploited, but there appear to be considerable economic possibilities in their development.

In the Scotch Carboniferous Limestone series are several useful fireclays; they occur chiefly at Prestongrange in East Lothian, Whitehill in Midlothian, and at Kingseat, Lochhead, Lilliehill, and Cardenden in Fifeshire. The clay at Kingseat is very plastic.

The Calciferous Sandstone series lying below the Hurlet Limestone also yields several beds of fireclay of fairly good quality. At Paisley, a fireclay seam 3 to 6 feet thick associated with the Ferguslie coal is worked. There are several other fireclays in the Dykebar Hill, Barrhead, and Hurlet areas, but little is known of them.

Slightly to the east of Barrhead two fireclays—one above and one below the Lower Arden coal, just under the Calmy (Carboniferous) Limestone—are used for firebricks and sanitary ware. In the Torphichen district a good seam of fireclay occurs immediately below the Cement Limestone.

The fireclays in association with the limestone have not been examined with sufficient thoroughness for their commercial value to be realised.

In chemical composition, the Scotch fireclays approach that of china clay more nearly than most English fireclays; the best specimens obtained from the "Old Mine" strata at Stourbridge resemble them, and though the average percentage of iron is greater in the Scotch clays, one of the Glenboig seams and Hurll's *Manuel clay* are notably low in iron compounds.

The **Irish** fireclays are chiefly found in County Tyrone. They are of No. 2 and inferior grades, but some are excellent for salt-glazed drain-pipes.

In **Wales,** fireclays are abundant (fig. 10), though it is not true to state, as has been done in several geological papers, that "every coal seam has a fireclay beneath it." The principal centres of the fireclay industry in South Wales are largely confined to Glamorganshire, and are mainly found in the vicinity of Pontypool, Risca, and Caerphilly on the eastern border of the coalfield, Beaufort on the north, Ystalyfera, Neath, and Llanelly in the Swansea and Tawe Valleys, and Brynamman, Ammanford, and Pontardulais in Carmarthenshire.

The fireclays of South Wales occur in three chief horizons: (i) the Upper Series, (ii) the Pennant Series, (iii) the Lower Series. The Upper series correspond to the Llantwit Coal Measures and the Mynyddislwyn series in Monmouthshire; the Pennant series lie below these beds; and the

Lower series extend to the Millstone Grit, in which the lowest beds of fireclay occur. Eight beds of fireclay of sufficiently good quality for the manufacture of firebricks and other refractory articles occur above the Mynyddislwyn coal in different districts. These beds vary from 2 to 6 feet in thickness, and are rather variable in quality; one 6-foot bed not associated with coal lies 225 yards below the Wernffraith coal, and deserves special attention on account of its resemblance to the Stourbridge fireclays. The clays in direct association with the Mynyddislwyn seams are of little value for refractory purposes, as they are very hard and siliceous, and frequently rich in sulphur and iron compounds.

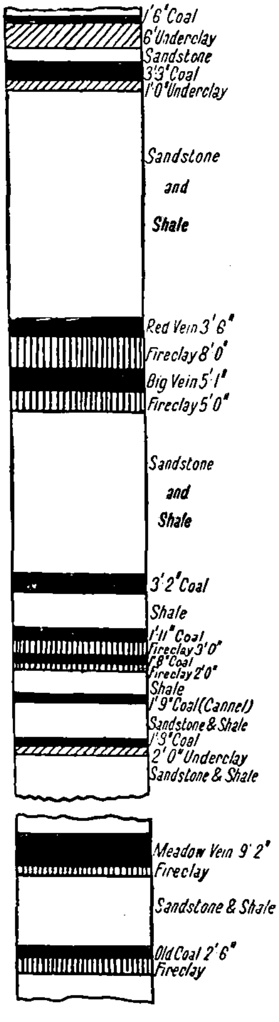

FIG. 10.—Section at Abersychan, S. Wales.

There are numerous seams of fireclay between the Mynyddislwyn and Rhondda No. 1 coals; most of them are too thin or irregular for use, though some of the fireclay in an 8-foot bed at Harris Steam Navigation Colliery and in a 4-foot bed in the Ogmore Fach is of good quality. The fireclay associated with the Rhondda No. 1 coal is not very refractory, seldom corresponding to Cone 32, and it is extremely irregular in character even in the same pit. Some of the beds might be useful for boiler settings and other inferior work, but the bulk of these clays are useless for the manufacture of first-class firebricks. Two beds of fireclay, 4 feet and 6 feet respectively, occur between the Rhondda No. 1 and No. 2 coals, and are accessible at Lady Lewis, Merthyr, Maritime, and Cwm Collieries, but they have not been adequately examined.

The fireclays associated with the Rhondda No. 2 coal are not, as a whole, of great heat-resisting power, their refractoriness varying from Cones 21 to 30, though portions of the beds are of much better quality, but are so mixed with useless material that they cannot be obtained in large quantities, and the cost of purifying is excessive. There are also several good fireclays at Abergwerelech, above the Blewers and Brown coals.

In the Lower series, some excellent fireclays occur between the Rhondda No. 2 coal and the Hughes Vein, the best being found at Cwm Gorse near Brynamman, in the Llanelly and Swansea district, where it is comparable to the Stourbridge clays. This clay occurs about 30 feet below the Red Vein coal, and other clays associated with this vein have been used for many years at Daren brickworks, in the Newport district, for the manufacture of first-class firebricks. Some of the thick shales at Cwm Gorse, about 200 feet below the Red Vein coal, are used for making ladles employed in steel-melting, etc.

At Caerphilly, in the Monmouthshire district, a fireclay which occurs in a 4-foot bed immediately beneath the Big Vein coal is mixed with the Red Vein clay when obtainable, though at Caerphilly the latter is mixed with shale and is very impersistent. At Lower Cwmtwrch, in the Llanelly-Swansea district, is a bed of 9 feet of fireclay beneath the Four-feet coal, which is used for firebricks and steel ladles; and beds of shale 16 feet and 30 feet respectively are used for various purposes as refractory materials in some of the local steel and spelter works.

A good, though siliceous, fireclay is found in Ebbw Vale, 12 yards above the Elled Vein and beneath the Oldham coal, and at Abercwmboi Colliery, in the Pontypridd district, there are three beds of good fireclay having a total thickness of 10 feet 6 inches, and occurring respectively 34, 27, and 21 feet above the Elled Vein.

The Ras-las or Black Vein coal is associated with several fireclays varying from 2 to 7 feet in thickness, but they are extremely variable in character and of inferior quality. The fireclays below the Ras-las Vein include some of the best in South Wales, those in the eastern part of the coalfield being the most accessible. Useful seams occur near Aberkenfig, Beaufort, Ebbw Vale, Bryncoch, Daren, Rudry, and elsewhere. These clays are used for the manufacture of firebricks, furnace linings, etc., and whilst not so refractory as the Stourbridge and some Scotch clays, they are sufficiently good for many purposes, if carefully selected, and those portions of the beds which are rich in pyrites are avoided.

Several fireclays are associated with the Old coal near Ebbw Vale, and a 6- to 10-foot bed of fireclay which occurs 8 feet above the Old coal at Beaufort has been used for the manufacture of firebricks, and two clays at Pontnewynydd —one 6 feet thick which occurs immediately above the Old coal, and the other 2 feet thick immediately below it—are mixed together for the manufacture of firebricks. At Llantarnam and elsewhere, the Lower of these clays appears to attain a thickness of 5 to 8 feet, but its character is very variable, and at Henllys it is replaced by a fine-grained quartz rock.

A 60-foot bed of fireclay, the relative position of which is uncertain, is worked at Darren, near Risca, the upper half being used for high-class firebricks and the lower half for inferior ones.

The Hard Vein clay is used in some places for the manufacture of sanitary ware, sewer pipes, and firebricks. At Gnoll Colliery, in the Swansea district, 6 feet of fireclay occurs between the Hard Vein and the Granway Vein in the Pennant series.

The Welsh fireclays in the Millstone Grit series have been worked fairly extensively in the past in some localities, including Pen-yr-alleg. The most important of these fireclays is a 2-foot 6-inch seam near Risca associated with the Sun coal, but even this is very irregular in composition.

The fireclay which occurs in the Carboniferous Limestone formation is not of commercial importance, being of low refractoriness and inaccessible.

The fireclays of South Wales are very variable in character, and are seldom above No. 2 grade, though specially selected strata yield clays of high quality. Among the best are the Cwm Gorse clay, previously mentioned as situated below the Red Vein, and the Risca clay beneath the Brass Vein. Each of these clays contains up to 60 per cent. of free siliceous material not in the nature of clay. The fine portion of these clays, obtained by elutriation, consists of clay, together with minute flakes of secondary mica and insignificant proportions of crystals of iron and titanium compounds. With care in selection, a much better average quality of fireclay could be used in this area, but hitherto the clays have been sent to the surface without selection, so that only medium quality bricks could be produced. This is due to the custom in Welsh collieries of regarding fireclays as waste products from the collieries rather than intrinsically valuable materials. In many respects, the fireclays of South Wales resemble those of the Midlands, but are somewhat more siliceous.

In **North Wales,** the useful fireclays are largely confined to Flintshire and Denbighshire, the works in Flintshire being located around Mold, Ewloe, and Buckley, and those in Denbighshire in the neighbourhood of Ruabon and Wrexham.

The Buckley fireclays occur in a broad, shallow syncline whose axis extends from Flint by Northop Hall and Ewloe Green in a south-easterly direction, forming two main outcrops. Six distinct beds are recognised, viz.—

(*a*) Purple shaly clay with local developments of pale green clayey shales and thin quartzose sandstone.

(*b*) Sandstone, massive, quartzose, fine-grained, usually yellowish white, but rather felspathic and pinkish in some of the higher beds, forming a well-marked bed and weathering with a purplish-brown crust, with subordinate beds of shale and fine-grained white siliceous clunch. This passes down into

(*c*) Siliceous clay or silt-rock, greenish white, very fine grained and sporadically developed; or sometimes mixed with

(*d*) Mottled purple clay, usually split up by a bed of white siliceous clunch. This is termed " Blue " clay.

(*e*) Shaly clay, dark grey or black, sometimes with thin coal seams; replaced northward almost entirely by red and grey blotched warrant and (locally) quartzitic sandstone.

(*f*) Coal, thin, becoming a mere streak of carbonaceous shale towards the north.

These materials vary greatly in composition—sometimes without change in their appearance. They are also richer in iron compounds (both ferric and ferrous oxide) than is usual in fireclays, the total iron oxide averaging about 5 per cent.

Buckley firebricks are burned in a reducing atmosphere and so are partially vitrified. For this reason, they are highly resistant to abrasion and corrosion, and to sudden changes in temperature. They also have great mechanical strength (3900 lbs. per square inch), but their refractoriness (Cone 30) is rather lower than that of many other firebricks. For many purposes, their other properties more than counterbalance the lower refractoriness. Buckley and Ewloe are famous for goods with peculiarly high resistance to acids as well as for refractory bricks. Near Mold, fireclays occurring in pockets in the Mountain Limestone, and similar to the pocket clays of Derbyshire and North Staffordshire, are worked.

The Denbighshire fireclays associated with the Stone coal are raised at Ruabon and Smelt, near Brymbo, those associated with the Half-yard coal and two coals above the Nant coal are raised at Delph, Ruabon, and those associated with the Llwyneinon Half-yard coal are raised at Rhosllanerchrugog. The underclay of the Chwarele coal is used at Garth, Trevor. These and a number of other underclays have never been sufficiently examined for their true value as fireclays to be appreciated.

A soft grey fireclay, 4 feet 6 inches thick, of unusual character for this district, occurs at Llay Hall, near Wrexham. It contains 49·5 per cent. of silica, 32·5 per cent. of alumina, 3·1 per cent. of ferric oxide, and has a refractoriness equal to Cone 33; this appears to be worth further investigation with a view to commercial development.

Some of the fireclays of North Wales bear a close resemblance to the better qualities of those obtained from the Northumberland and Durham coalfields.

Bastard fireclays are the clays associated with coal seams (underclays) which are not sufficiently refractory to be used for the manufacture of firebricks, etc. Seams of such clays occur in almost every coalfield and beneath almost every seam of coal. The better qualities are largely used in the manufacture of salt-glazed ware, building and engineering bricks, sanitary ware, coarse pottery, and for all purposes where a high degree of refractoriness is not required. They are, in many cases, eminently suitable for the production of " stoneware," as they form a vitrified and impermeable ware without the tendency to twist and warp shown by more readily fusible clays.

Within the compass of a single volume it is impossible to give complete details of all the fireclay seams, owing to their sudden and serious variations within small areas. Tables of strata are published in various *Memoirs of the Geological Survey*, but with few exceptions these afford little or no information as to the value of the fireclays[1] tabulated, so that it is necessary to test each stratum thoroughly before its value can be known. Even then, the liability to sudden variations in composition necessitates the most constant vigilance and oversight, or the clay may be spoiled by admixture with a less refractory material.

It is highly probable that fireclay deposits of great value are still unworked in various parts of the country. This is largely due to ignorance respecting their qualities. In more than one instance colliery owners have discarded as useless large quantities of very valuable fireclay, which have brought in large profits as soon as the material was utilised. There is a tendency on the part of many colliery engineers to overlook the value of fireclays and to devote the whole of their attention to the coal. Consequently, there are many valuable fireclays the existence of which is scarcely suspected by those to whom they would be the most profitable. Defective methods of sampling and testing the clays are also responsible for valuable clays being overlooked.

The disastrous consequences resulting from the use of insufficiently refractory materials in large industrial furnaces make it imperative that the risks should be reduced as far as possible. Hence, firebricks and other refractory goods are sold chiefly " by reputation." One result of this is to bring the fireclays of a small number of localities into great prominence, whilst those in other districts remain practically unknown outside the area where a local use is found for them, though they may be quite as refractory and valuable as the more popular clays.

Fireclays from different sources differ greatly in composition, and the various parts of the same seam are by no means exactly alike. Broadly speaking, they are all alumino-silicic acids[2] richer in silica than the kaolins, and usually containing free silica, together with the various minerals described on p. 67 *et seq.*

As different parts of a seam will yield different results on analysis, it is obvious that the publication of analytical figures for fireclays is of very limited value, but the ones shown in Table IX. are as typical as any such figures can be. A comparison of the data in the table will readily show what large differences occur in clays from the same locality.

The great variation in fireclays from the same locality and from different seams in the same pit is shown in Table X., the analyses in which were made by E. P. Page.

Large differences in the results of chemical analysis are often obtained when a carefully selected sample is compared with a random piece taken without any precautions. It is, therefore, of great importance that samples should be properly taken so as to be representative.

[1] Many of those which the author has examined were found not to be fireclay but soft siliceous rocks which readily hardened on exposure. The arrangement by which the shaft-sinkers are paid, according to the nature of the material through which the shaft is sunk, appears to be the cause of many false entries with respect to fireclay. Further errors are due to the custom of recording all soft materials immediately below a coal seam as " fireclay ! "

[2] The oft-repeated statement that fireclays are " silicates of alumina " is misleading, inasmuch as such a term implies a neutral substance, whereas fireclays are acids.

TABLE IX.—TYPICAL ANALYSES.

District.	Clay.	Silica.	Alumina.	Iron Oxide.	Lime.	Magnesia.	Soda + Potash.	Water, etc.
St Austell	China clay	46	39	..	0·5	..	0·5	14
Dorset	Ball clay	49	32	2	0·5	..	3	13·5
Devonshire	,, ,,	48	36	0·5	1	..	1	13·5
Stourbridge	Fireclay	65	22	2	0·5	..	0·5	10
Scotland, Kilmarnock	,,	52	28	1·5	0·5	0·5	1·5	16
,, Glenboig	,,	46	36	2	..	..	0·5	14·5
,, Bonnybridge	,,	49	33	1	0·5	1	2	14
Northumberland	,,	60	28	2	1	..	2	7
Durham	,, (mild)	52	32	3	0·5	0·7	1·5	10
,,	,, (strong)	62	25	1	0·1	0·5	1	10
Stannington	,,	48	35	3	1	1	1·5	10
Derby	,,	52	36	2	1	0·5	1	8
Church Gresley	,,	46	36	2	1·5	0·5	2	12
Cattybrook, Bristol	,,	60	21	5	0·5	0·7	2	9
Chester	,,	59	28	3	0·5	0·5	..	9
Buckley, N. Wales	,,	81	12	2	1	..	3	..
Leeds	,,	71	20	1·5	0·5	..	1	6
Halifax	,,	71	19	0·5	0·5	0·5	0·5	8
South Midlands	,,	59	29	2	1·5	0·5	1	8
Teign Valley	,,	77	17	2	..	..	..	4
Turton Moor	,,	59	29	1	1	..	..	10
Dowlais	,,	67	21	1·5	0·5	0·8	2	7
Shropshire	,,	59	27	1	0·5	..	0·5	12
Glamorgan	,,	67	20	2	1	1	5	4
Ayrshire	Bauxitic	40	44	1	1	..	1	13
Ewell, Surrey	Loam	88	4	5	1	..	1	1
Staffordshire	Peacock fireclay	64	26	1	..	0·5	..	8
,,	Bassey Mine marl	63	21	3	0·5	1·0	3·2	8
,,	Sneyd marl	76	16	2	..	..	..	6
,,	Hanley sagger marl	62	29	3	1	..	..	5
Sheffield	Ganister	89	4	3	3	..	1	..
Laisterdyke, Yorks	,,	97	1·5	0·8	..	..	0·5	..
Bonnymuir, Scotland	,,	89	5	3	0·5	0·2	..	2
Glamorganshire	Dinas	98	1	1	..	..	..	..
Medina, U.S.A.	Quartzite	98	1	1	0·1	0·2	0·4	..
Baraboo, ,,	,,	97	1	1	0·1	0·3	0·1	..
Alabama, ,,	,,	98	1	1	0·1	0·3	0·3	..
Westerwald, Germany	Findlings Quartzite	98	2	0·4	0·1		n.d.	..
Saxony, ,,	,, ,,	97	1	0·5	0·3		n.d.	..
Hesse, ,,	,, ,,	98	2		n.d.		n.d.	..
Derbyshire	Limestone Pocket clay	81	11	1	1	..	2	4

Note.—Very small proportions are purposely omitted so as to facilitate comparison. Under 2 per cent. of titanic oxide is present in most of the fireclays; in the table it is included in the figures for silica and alumina. The foregoing figures differ considerably from single analyses made of the materials mentioned, because most refractory materials vary considerably even when obtained from the same bed.

An extensive study of the analyses of a very large number of Coal Measure fireclays from various parts of the world led W. and D. Asch to conclude that the alumino-silicic acids which form the chief constituent of each are substances with the following or analogous formulæ:—

$H_4Al_6Si_{12}O_{35}$. $H_4Al_6Si_{15}O_{41}$. $H_4Al_{12}Si_{12}O_{44}$. $H_4Al_{12}Si_{16}O_{52}$.
$H_4Al_6Si_{10}O_{31}$. $H_4Al_6Si_{18}O_{47}$. $H_4Al_{20}Si_{12}O_{56}$. $H_4Al_{12}Si_{18}O_{56}$.

TABLE X.—BURNED STOURBRIDGE FIRECLAYS.

	Silica.	Alumina.	Iron Oxide.	Lime.	Magnesia.	Soda and Potash.	Refractoriness (Seger Cone).
1.	70·7	25·8	2·4	0·3	..	0·8	30–31
2.	73·8	20·5	4·4	0·1	..	0·1	28
3.	53·9	43·2	2·1	0·1	0·3	0·4	34–35
4.	73·1	21·7	3·5	0·4	0·3	1·0	28–29
5.	68·6	26·1	3·8	0·4	0·3	0·8	29–30
6.	74·4	20·6	3·1	0·4	0·2	1·2	27–28
7.	67·5	27·9	2·6	1·2	1·2	0·3	..

TABLE XI.—STOURBRIDGE CLAYS.

	Best Selected Stourbridge Old Mine.	Ordinary Stourbridge Old Mine.	Selected Clay for Glass Pots.
Silica	76·5	56·6	60·5
Alumina	16·5	26·5	26·3
Iron oxides	0·8	2·3	1·9
Lime	0·1	0·2	1·1
Magnesia	Trace	0·3	0·7
Potash and soda	0·7	1·7	1·1
Loss on ignition	5·1	12·0	8·2

The variations in the composition of fireclays from the same coalfield are still more clearly shown in the following more detailed analyses by A. A. Hall:—

TABLE XII.—NORTHUMBRIAN FIRECLAYS.

	A.	B.	C.	D.	E.	F.	G.
Moisture (loss at 110° C.)	1·97	1·60	1·80	2·10	2·00	2·10	2·20
Organic matter and water . . .	6·00	10·60	5·30	9·40	8·10	8·00	7·75
SiO_2	63·69	55·44	65·55	54·26	56·00	56·10	56·20
Al_2O_3	23·01	25·31	21·21	29·02	29·08	29·28	29·25
MnO	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Fe_2O_3	2·40	2·30	2·00	1·80	1·70	1·80	1·70
P_2O_5	0·03	0·03	0·03	0·05	0·02	0·02	0·02
TiO_2	1·18	1·23	1·21	1·14	1·17	1·14	1·15
CaO	0·65	0·62	0·50	0·75	0·88	0·80	0·75
MgO	..	0·50	0·00	0·08	0·08	0·10	0·09
K_2O	1·08	1·80	1·50	1·29	1·08	1·00	1·01
Na_2O	0·25	0·40	0·98	0·20	0·15	0·09	0·10
	100·26	99·83	100·08	100·09	100·26	100·43	100·22

A and B are from Corbridge. C is from High Shield, Hexham. D to G are from Lambton Colliery Main Seam, the samples being taken at varying depths.

If a sample of fireclay is carefully treated with water so as to remove all the coarser particles, and the finer particles are then analysed, its composition will usually coincide—within narrow limits—with one of these formulæ. Unfortunately, the very wide variations in the composition of contiguous parts of the same seam are so great as to make any attempt at exact classification futile until some better method of investigation can be adopted. At present the impossibility of knowing whether a sample of fireclay has been wholly freed from adventitious impurities prevents very exact investigation of their true chemical constitution. At the moment, it is only possible to state that fireclays possess the characteristic properties of crude alumino-silicic acids, but the precise composition of the acid forming a particular fireclay is largely a matter of conjecture.

In judging the quality of a fireclay and its suitability for specific purposes, a chemical analysis is of little value, and unless carried out with exceptional care it may even be misleading. Beyond indicating the total amount of bases forming the impurities which lower the refractoriness of the clay, and affording a rough indication as to the amount of free silica in the material, a chemical analysis alone gives little information, and should be supported by physical tests and observations on the refractoriness, colour, texture, cleavage, markings, and other special features of the material. The chief value of a chemical analysis, however, is to show the proportion of potash, soda, lime, magnesia, iron oxide, titanium oxide, and any other substances which may have a detrimental effect on the refractoriness of the clay.

In comparing fireclays, less regard should be paid to the results of chemical analysis than to the refractoriness as judged by a heating test. It must also be borne in mind that for some industrial purposes a clay which is less heat-resisting than another may yet be superior in its general durability, because it possesses a greater resistance to corrosion by slags, abrasion, etc.

The **impurities in fireclays** are numerous, and have an important influence on the chemical and physical properties of the clay, though the total percentage of impurity in a useful fireclay can never be large. In fact, an essential difference between fireclays and brick—or stoneware—clays is that the latter depend for their distinctive qualities on the iron oxide and other fluxes[1] which they contain, whilst the refractoriness of fireclays is due to the absence of more than unavoidably small proportions of such impurities.

A study of these impurities is made all the more complicated by the fact that part of the silica and alumina in clays actually constitutes the clay itself. Hence, it is very necessary to consider the mineralogical form in which the impurity occurs, as well as the actual proportion of one or more of its constituents. Thus, an analysis may show the presence of 2 per cent. of soda or potash in a fireclay, but the impurity (say felspar) of which this soda or potash is one constituent may be present to the extent of more than 12 per cent.—a proportion which may be serious.

Silica.—The silica present in a fireclay may be in one or more of four forms: (*a*) combined with alumina and water to form clay; (*b*) as hydrated silica; (*c*) as free silica, quartz, "sand," or flint; and (*d*) as silicates (felspar, mica, etc.).

Only the forms (*b*), (*c*), and (*d*) can be regarded as impurities, and a certain proportion of silica in form (*c*) is often essential in the commercial usage of refractory clay, as it forms the bulk of the coarser particles which make a kind of skeleton and prevent cracking and excessive shrinking. Hence, the word "impurity," as applied to silica in a fireclay, does not necessarily indicate that a clay would be increased in commercial value if the free silica could be removed.

[1] The term *flux* is applied to any material which reduces the fusing-point of a clay to which it is added. It usually refers to lime, magnesia, soda, and potash and their compounds, but has a much larger meaning, and may include almost any impurity present in a fireclay.

The proportions in which these various forms of silica may occur are shown in the following analyses of four fireclays:—

	No. 1.	No. 2.	No. 3.	No. 4.
Silica, free, as sand	56·95	47·4	29·63	16·2
„ combined with bases and as clay	18·69	26·98	37·74	45·53
„ as hydrate	1·39	1·06	0·91	1·05
Total silica	77·03	75·44	68·28	62·78

Unfortunately, the difficulties of analysis make it necessary to accept such figures with caution, especially as some of the silica reported as " free " may be in the form of a micaceous or felspathic sand; much of the silica reported as " combined with bases " is in the form of clay (alumino-silicic acid), and the remainder of felspathic or micaceous matter; and some of that reported as " hydrate " may have been formed during the analysis by the action of sodium carbonate. It will thus be seen that it is almost impossible to separate these forms of silica with great accuracy, though they may all be known to exist in a given clay.

Silica occurs as " soluble silica " and "insoluble silica," and intermediate between them is " colloidal silica sol," in which the silica is in suspension in so finely divided a state that it may easily be mistaken for " soluble silica." The " insoluble silica " may be in the form of relatively coarse particles of " sand," or in the much finer precipitated state known as " hydrated silica." When freshly prepared, the latter readily combines with caustic alkali or lime in aqueous solution, but the coarser " insoluble " form is only attacked by these solutions if it is in a sufficiently finely powdered condition. Extremely finely divided silica will react with boiling water, forming colloidal silicic acid; a large proportion of colloidal silica reduces the refractoriness of a highly refractory clay, and increases the shrinkage on drying of all clays which contain it, but "insoluble silica" usually reduces the shrinkage. The soluble form of silica is made insoluble on heating to 105° C., at which temperature it is coagulated, and can only be redissolved with great difficulty.

Colloidal silica, containing up to 90 per cent. of water, occurs to a small extent in some clays both in the form of a sol and of a gel. The former may be extracted by water, and the latter by boiling with a very dilute solution of sodium carbonate. It differs from many organic colloidal gels in possessing little elasticity, so that it does not materially enhance the plasticity of the clay in which it occurs. For further information concerning the properties of colloidal silica see p. 154.

The product obtained by mixing lime with colloidal silica sol appears to be of great importance in the manufacture of silica bricks; on heating, it is converted into calcium silicate.

The *hydrated silica*[1] mentioned above is of little commercial importance. It was at one time thought to be important in the manufacture of firebricks, in which lime was used as the cementing medium, but it has now been conclusively proved that so long as there is sufficient silica in an extremely fine powder present, there is little or no advantage in its being in a hydrated condition.

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[1] " Hydrated silica " occurs usually in the form of a colloidal gel, and may properly be considered as " colloidal " silica.

The forms in which "uncombined silica" occurs most frequently in clays are: (i) amorphous silica, including chalcedony, flint, and chert, and (ii) crystalline silica, *i.e.* quartz, etc.; the latter, with a certain amount of siliceous material, forms the stony and sandy portions of many clays. It may be removed to a large extent by exposing the powdered clay to a very slow stream of water, or by stirring up the material with water or, preferably, a very dilute solution of sodium carbonate (as described in Chapter II.), and pouring off the supernatant liquid after it has been allowed to stand for a few minutes. Neither of these methods effects a complete separation of the silica, as the finest particles of it are carried away with the clay.

Quartz, being devoid of plasticity, its chief effect, when mixed with clay, is to act as a dilutant of the clay, reducing its shrinkage on drying and heating, and making it "short" or "lean." A suitable proportion of quartz is, therefore, a useful constituent in some cases, as it facilitates the moulding and drying of articles made from the clay, and also promotes the chemical reactions required in the vitrification of the ware. For the latter purpose, the quartz must be in a very finely divided state, and in no case should the proportion be excessive, or it may produce a brittle ware of poor strength and feeble wearing qualities.

Sand[1] is a term used to indicate small grains of silica in the form of quartz or quartzite, or of other minerals of a highly siliceous character. It is valued according to the percentage of silica it contains, very small amounts of other ingredients considerably reducing its worth for glass-making and other manufacturing purposes. Sand is derived from a large variety of rocks, and may, in a broad sense, be regarded as naturally occurring powdered rock, of indefinite composition, produced by the action of weather, rivers, seas, etc. This term may thus be used to include numerous minerals in clay and other deposits, whose chief characteristics are their granular form, their hardness, and freedom from plasticity. These particles vary very greatly in size: those larger than $\frac{1}{20}$ inch in diameter are usually termed *shingle*, *stones*, or *gravel*; those less than $\frac{1}{250}$ inch in diameter are termed *silt*, though in some cases the minimum size of sand grains is taken as $\frac{1}{200}$ inch, anything smaller than this being termed *dust*. A further distinction is made with regard to the rounded particles or *pebbles* and the sharp, angular particles of more recent formation, the latter being preferable to rounded grains in clay-working, as they interlock more completely with each other and so produce much stronger articles.

Owing to the wide sense in which the term "sand" is used, the composition of this material is exceedingly variable. The purest sands consist almost wholly of silica, but some sands contain only 40 per cent. of this oxide, the other constituents being limestone, or combined silica in the form of felspar, mica, and other mineral silicates and alumino-silicates. These are detrimental to the heat-resisting power of clays in which they occur. This is due to the fact that such felspathic and micaceous sands introduce alkalies (which act as fluxes) as well as silica, and may seriously alter the properties of the fired goods, causing the latter to vitrify at a lower temperature or even to lose their shape before the firing is completed. For some refractory articles, including porcelain, only the purest sand can be used, but for lessening the plasticity of brick and terra-cotta clays, less pure sands are equally satisfactory if they are sharp and "clean." When a pure sand is not obtainable, one containing grains of felspar is preferred to a sand containing lamellar spangles of mica, as the latter—being very thin—are more easily affected by the heat, and, therefore, exert a much

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[1] For further information see the author's *Sands and Crushed Rocks* (Frowde, Hodder & Stoughton).

more corrosive influence than the more spherical and less easily fused grains of felspar.

The fusibility of sand is somewhat difficult to determine. Probably the best way is to make it into a paste with water containing a little dextrin, and from this to form cones which are then heated along with Seger cones in a kiln or special furnace, and the relative behaviour compared with a good sand similarly treated. This method of testing is similar to that used for clays, and is fully described later.

Flint is a form of free silica which does not usually occur in clays—except in the commercially useless "clay-with-flints" which is associated with some parts of the Chalk formation—but it is sometimes artificially mixed with them. For further information see p. 152.

In all its forms, pure silica is a highly refractory material, being almost as infusible as the best fireclays when heated alone. If it contains lime or other bases, however, it melts much more easily.

Sand in Clays.—The proportion of extraneous silica (whether as quartz, quartzite, flint, sand, or as a constituent of another mineral) in clays is important, yet it varies enormously. The purer china clays are almost free from it, but some "clays" used for brickmaking contain as much as 95 per cent.

In studying the reports of the analyses of a clay, the fact must not be overlooked that true clay[1] contains rather more silica than alumina, and that in endeavouring to estimate the approximate composition of a given sample a deduction must be made from the "total silica" in the report, to account for that combined with the alumina and alkalies present. Thus, a fireclay containing 25 per cent. of alumina and 65 per cent. of silica will probably not contain more than 25 per cent. of uncombined silica.

It is sometimes stated that all the silica in a fireclay in excess of 45 per cent. is usually free silica, although it may be in such a fine state of subdivision as to be impalpable. This is not strictly correct, as in the form of felspar and mica much higher percentages of combined silica may be present. Moreover, there is evidence to show that some fireclays are alumino-silicic acids which are richer in silica than is china clay or kaolinite, from the composition of which the above statement is derived. This may be expressed more clearly by stating that china clay is an alumino-silicic acid of the type $H_{4x}Al_{2x}Si_{2x}O_{9x}$, whilst the Coal Measure fireclays are of the types shown on p. 65.

A fireclay containing a large proportion of silica is not of necessity a good fireclay, though it is a common error to suppose this. Indeed, the extra silica is more often a source of weakness, for a brick may be too friable and mealy, and may lack tenacity to such a degree that fierce draughts in a furnace will carry it away particle by particle. Again, the uncombined particles are more easily surrounded and attacked by the fluxing elements found in all coals, forming slag spots.

Many persons, even those engaged in brick manufacture, make the error just mentioned of assuming that a brick rich in silica is necessarily a good one, because *silica* bricks are largely used for refractory linings in furnaces. In reality, no direct comparison of the composition of silica bricks with fireclay bricks is possible. Indeed, Seger has shown that the addition of silica to the purest clays reduces the refractoriness. Moreover, it is well known that highly siliceous clays are restricted in their uses, as they are liable to failure through combination of the free silica with the oxides of iron and

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[1] Assuming that all *true clay* has the same percentage composition as kaolin, etc., which is by no means necessarily the case, as explained on p. 6.

other fluxing agents in the material treated in the furnace. The power of combining in this way varies with their condition and origin, the amorphous variety of silica, especially when in a jelly-like condition, being the most readily, and crystallised quartz in somewhat large pieces being the least, affected.

The behaviour of silica in the kiln largely depends on the form it assumes, and it is less important to know how it is combined. Free silica is infusible, except at higher temperatures than those obtainable by the clayworker in the ordinary course of his work, but any impurities with which it may have become mixed reduce the temperature at which it melts.

Briefly, the chief effect of adding silica to a plastic clay is to reduce its plasticity, shrinkage, tendency to warp and crack, the amount of water required to make it plastic, and the tensile and crushing strength, and to increase its porosity after firing. The addition of free silica will also reduce the refractoriness of a fireclay relatively free from fluxes, though the ability of the latter clay to withstand sudden changes in temperature may be increased. This is due to the fact that *free* silica, though of itself extremely refractory, readily combines with oxide of iron, alkalies, and other bases present as impurities, to form fusible silicates. Common glass, composed of silica and soda or potash, melts completely below 1500° C., and is a familiar example of a silicate, just as slags—which are more fusible—are the corresponding clay products.

When the presence of a certain amount of sand does not interfere with the desired properties of the product, a small amount may be very usefully added prior to grinding a plastic or sticky clay, because such clays are often very difficult to grind alone, as they tend to slip on the rolls and so waste power, but when sand is added to them the grinding is facilitated.

When much silica is present, the amount of water required to convert the clay into a good modelling paste is reduced, and the drying of the articles made from it is greatly facilitated. Silica is largely used for the prevention or reduction of shrinkage, and is added in the form of crushed rock or sand to bricks, tiles, and coarse pottery, and as ground flint to white ware. A great excess of silica must usually be avoided, as it tends to expand when heated to a high temperature and to cause cracks in the ware.

The size of the grains of silica is important. In an impalpable condition silica is most objectionable, but if in larger grains or crystals, it less readily enters into hurtful combinations with fluxing agents. The larger the grain, the more difficult is it to melt or dissolve it, and frequently the outside of a grain of quartz will be melted while the inside remains unaffected. In the time occupied in burning most refractory articles, only the finest particles of silica can enter into combination and so act as a flux, but at higher temperatures, or on very prolonged heating, to which some firebricks, etc., are subjected when in use, much larger particles may enter into combination and so gradually effect the destruction of the articles containing them.

There is much confusion of thought with regard to free and combined silica ; the facts may be summarised as follows :—

Free silica added to a perfectly pure clay will, within certain limits, reduce the refractoriness of the clay. If the clay is very impure, the addition of free silica may increase its refractoriness, though it can never make a fusible clay really refractory. (See fig. 29, and Tables XLIII. and XLIV.)

Combined silica, if in the form of an alumino-silicic acid (clay), is almost infusible, but if other oxides are also in combination with the silica the compounds formed will be more fusible. Thus, felspar—in which silica is combined with alumina and potash—is a well-known fusible mineral. Generally speaking, the other compounds of silica are more fusible than the alumino-silicic acids (true clays), most of which have a great resistance to heat. The adventitious alumino-silicates (such as felspar and mica) vary greatly in their effect on the fusibility of the clays containing them. Thus, weight for weight, mica is a far weaker and slower flux than felspar.

The effect of the presence of free or combined silica in a clay, or added to a clay, must depend entirely on the other substances present, and on the nature of the silicon compound itself.

Fortunately for the maker of refractory goods, it is seldom necessary to distinguish between the different minerals present as coarse particles, the terms sand, gravel, and stones being sufficiently comprehensive, but the finer particles need more detailed consideration.

Their nature must usually be recognised by their microscopical and chemical characteristics, though the peculiar, glistening, frost-like particles in many clays usually afford a ready means of detecting even small quantities of mica.

Alumina (Al_2O_3), like silica, occurs naturally in all clays: (*a*) in combination as an essential constituent of alumino-silicic acid; (*b*) in combination as alumino-silicates, in which form it is an " impurity "; and (*c*) in the free state. Free alumina is, however, seldom observed in raw clays, though, according to Van Bemmelen, it occurs in some tropical clays in the forms of *laterite* and *hydrargillite*, $Al(OH)_3$, both of which are decomposition products of diorites and granites.

Apart from its normal occurrence in alumino-silicic acid, the chief forms in which alumina occurs in clays are felspar, mica, hornblende, and tourmaline, and various other alumino-silicates derived from igneous rocks. A large proportion of these alumino-silicates may be removed by washing the softer clays, but no method has yet been devised for effectively separating them from a shale or indurated clay.

The effect of adding free alumina (either artificially prepared or in the form of native *bauxite*) to a clay is similar to that of adding free silica, but a somewhat more refractory material is produced, and clays rich in alumina are apparently more viscous, and so retain their shape well when heated to the softening point. A mixture of bauxite and fireclay containing equimolecular parts of alumina and silica will, if heated to a temperature of 1250° C. to 1400° C., form crystals of sillimanite ($Al_2O_3.SiO_2$) on cooling, the felted mass being particularly strong and resistant to sudden changes in temperature.

Compounds of alumina, other than clays, appear to reduce the plasticity and to increase the fusibility, impermeability, and strength of the clays to which they are added; but this statement is too general to be entirely accurate, and presupposes firing at a sufficiently high temperature. With underfired goods, the alumina compounds other than clays act simply as non-plastic materials. For further details see under " Refractoriness."

Iron Compounds.—No natural clays are entirely free from iron compounds, and even the most stringent attempts at purification do not succeed in removing all the iron present.

The chief compounds of iron occurring in clays are the two oxides (more or less hydrated), the carbonates, sulphides, and various minerals containing iron as an essential constituent, such as glauconite, ilmenite, etc. They are derived from decomposed ferruginous rocks, either by direct admixture or by their becoming dissolved by organic acids and the solution penetrating into the clay and being decomposed later.

In the analysis of clay it is customary to report the iron compounds as though they were all present as the red oxide (Fe_2O_3), no distinction being made as to the forms in which the iron is actually present. As a matter of fact, the proportion of ferric oxide in a refractory clay is usually very small, the iron present being chiefly in the form of sulphide (as *pyrite*, *mundic*, or *marcasite*), with some carbonate (*siderite*) and hydroxide (*limonite*).

In spite of the thorough and careful investigations which have been carried out during the past fifteen years, the state or condition in which iron occurs in burned clay is still a matter of conjecture. The red colour of certain articles, such as bricks and terra-cotta, is apparently due to the presence of free ferric oxide, but this is by no means certain; and, in any case, the colouring particles must be extremely minute, as the addition of specially prepared iron oxide—no matter how finely ground—does not produce the same shade of colour. A better use of iron as a colour may sometimes be made by thoroughly mixing a solution of ferrous or ferric salt with the clay, and then precipitating the iron as ferric hydroxide by the addition of a solution of soda or ammonia. The process is too costly for general use and is by no means a certain one, as the precipitated particles must be extremely minute—almost colloidal—to produce satisfactory results. Hence, the precise form in which the iron is present in a clay is often the chief factor in determining the effect of such iron, as the oxides and carbonates tend to be disseminated throughout the mass and so give a uniform colour to the burned clay, whilst the sulphides and some silicates tend to form aggregations or spots in the burned ware. Moreover, whilst ferrous carbonate has a tendency to granulate, and so produce goods containing black or brown specks, being relatively soft, it will generally be found that a finer grinding of the material, with greater care in preparation, will remove the defect. With ferric sulphide (pyrite), on the contrary, the granules are never small enough to give a red colour to the clay, but invariably show up as black or slagged spots, even after passing through the finest sieves.

Reducing agents, such as carbon compounds, by virtue of their superior affinity for oxygen, prevent, or delay, the iron from playing its customary rôle, and consequently, may cause untold trouble in the burning. This is especially the case with the pyritic and bituminous fireclays, the sulphur in which acts as a reducing agent.

It is not usually sufficiently realised that iron compounds are more affected by the method of burning than by the actual proportion present, for, according to the way in which this is carried out, the products may be beautifully coloured and of pleasing shades, or they may be swelled up, deformed, rough, spongy, weak, and worthless. In this connection, it may be pointed out that an error made in the early stages of the firing can never be fully repaired later, so that if the iron oxide has been reduced by the carbon in the clay and afterwards been apparently fully oxidised, the clay never assumes the colour it would have had if heated in an oxidising atmosphere throughout.

In many fireclays, the greater part of the iron compounds is so finely divided and so well distributed that it merely stains the burned clay to a pale buff colour, but in some clays small pellets or larger nodules or "kidneys" occur, these last being particularly objectionable, as they are difficult to grind, and produce an uneven composition of the clay in which they occur. Where the iron compounds are in a sufficiently fine state of division and thoroughly incorporated throughout the clay, an even-coloured article may be produced; but this is impossible where they exist in distinct pellets or in larger pieces.

Taking the various iron compounds in turn, it should be observed that—

Ferrous carbonate ($FeCO_3$) occurs frequently in certain clays, chiefly in the form of concretionary masses or as a film coating other minerals, but occasionally as minute crystals (*chalybite*). The masses of this carbonate, known as *siderite* or *clay ironstones*, are present in many clays, but are most noticeable in the Staffordshire marls and the buff-burning fireclays of the Coal Measures. It must be removed before these can be used for some purposes, as when heated to a temperature of 400° C. to 450° C. it loses carbon dioxide, leaving ferrous oxide which forms characteristic black spots of a slag-like nature, which spoil the appearance and reduce the refractoriness of a fired clay. If, however, the atmosphere of the kiln is sufficiently oxidising, the unstable ferrous oxide is oxidised to red ferric oxide as soon as it is formed, and little or no harm may result. On exposure, ferrous carbonate loses carbon dioxide, and is converted into a hydrated ferric oxide, possibly *limonite*.

Ferrous sulphate ($FeSO_4$) sometimes occurs in moist clays, but only to a small extent. It appears to be retained by the clay, and cannot be readily removed by washing. It sometimes causes the formation of a bluish-green scum on the surface of dried goods. This can be avoided by the addition of a small quantity of baryta to the clay before mixing the latter with water and pugging. In most cases, however, the discoloration is not sufficiently serious to be objectionable. In the kiln, ferrous sulphate behaves in a similar manner to ferrous carbonate, from which, in the presence of clay, it is often difficult to distinguish it.

Ferrous oxide (FeO) occurs but rarely in clays, though it is sometimes produced in the kilns by the reducing action of the fire-gases on other iron compounds. It readily unites with silica and with clay to form a dark slag-like mass.

The most fusible mixture of ferrous oxide and clay has, according to Rieke, the formula $2FeO.Al_2O_3.2SiO_2$, corresponding to 39·2 per cent. ferrous oxide, 27·8 per cent. alumina, and 33 per cent. silica; it fuses at Seger Cone 3*a* (1140° C.). According to J. White[1] there are no ternary compounds, but three ternary eutectics: (*a*) FeO 32, Al_2O_3 3, SiO_2 65 per cent. (melting-point 980° C.); (*b*) FeO 68, Al_2O_3 3, SiO_2 29 per cent. (melting-point 1002° C.); and (*c*) FeO 72, Al_2O_3 3, SiO_2 25 per cent. (melting-point 1080° C.).

Magnetic iron oxide (Fe_3O_4) is seldom found in raw clays, but is occasionally produced when some clays are heated.

Ferric oxide (Fe_2O_3) is regarded as the cause of the buff colour in burned fireclays and of the characteristic red colour of common bricks. The colouring action of ferric oxide is very largely dependent on the presence or absence of other materials in the clay. Thus, if much lime is present, the red colour of the iron oxide is almost entirely destroyed, and a white- or cream-coloured article is produced by the combination of the iron with lime and silica. There is evidence that the iron which is commonly understood to be present as ferric oxide is, really, in the form of a ferro-silicic acid such as *nontronite* ($H_4Fe_2Si_2O_9$), though some hydrated ferric oxides ($Fe_x(OH)_y$) may be present.

On burning clay, the iron sulphides present are sometimes oxidised to ferric oxide, so that this substance is not infrequently found in burned fireclays, though in most cases ferric oxide is readily reduced to ferrous oxide on heating in a kiln with an insufficient supply of air. The reduced oxide usually combines with the free silica in the clay, producing a bluish-black or grey slag which forms the well-known black spots in burned firebricks. When heated with a sufficient amount of air, ferric oxide remains uncombined even at very high temperatures, and then produces the characteristic red colour of certain clay-wares. Hence, the iron compounds in fireclays are

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[1] *J. West of Scot. Iron and Steel Inst.*, 1937, **44**, 85.

important fluxes when reduced to the ferrous state in burning. This fact is often overlooked.

Ferric hydroxide, or hydrated ferric oxide, is not a single substance, but includes a wide range of combinations of ferric oxide with water. Its composition is capable of infinite modification, and is dependent on the tension of the aqueous vapour in contact with it. This explains the many variations in colour—from yellow to red—in goods made of clay. All ferric hydroxides behave like colloids; on being heated they lose water and are converted into complicated oxides of a composition similar to, but not identical with, the formula Fe_2O_3. The relative volumes of the different hydroxides have, apparently, some effect on the colour of the goods produced from the clays in which they occur.

Limonite is usually represented by the formula $2Fe_2O_3.3H_2O$, but, being colloidal, it may not possess a really definite composition. It is commonly understood to produce the yellow colour in many surface clays and weathered shales. It occurs evenly throughout the mass, and also in irregular nodules or "kidneys," particularly in weathered clays. These may usually be removed by hand, but if left in the clay they cause irregularity of colour.

When ferric oxide and the various ferric compounds are exposed to the action of the weather, limonite or other ferric hydroxides are produced.

Magnetite (Fe_3O_4) is a black oxide of iron rarely found in raw fireclays, but is produced from the ferric oxide when they are burned. As its name implies, it is magnetic, and may be detected by its influence on a compass needle.

Vivianite, a crystalline ferric phosphate, has been found in some boulder clays as tiny blue specks, but the amount is too small to be determined.

Ferric sulphide (FeS_2)—*pyrite*—occurs in clays in several forms of the same chemical composition as *pyrite*, *mundic*, and *marcasite*. These occur chiefly in the shales of the Coal Measures, but are also found in ball clays, and are apparently formed by the action, on ferrous carbonate, of sulphuretted hydrogen evolved from decomposing organic materials, possibly with the aid of bacteria. These sulphides may be disseminated in the clay, but are usually found in groups resembling petrified roots, or in nodules or "kidneys," though in some clays and shales *pyrite* occurs as cubical crystals resembling minute blocks of polished brass, this brassy lustre being very characteristic. These crystals are particularly noticeable in coal-pit refuse (shales), which is largely used for brick-making in some districts. When the nodules are large they are easily removed; when they are small and numerous they are difficult to separate. For coarse articles they may be often left in the clay, though they then form cavities and a blackish slag of iron silicate.

Marcasite is chiefly found in twin rhombic crystals, fibrous masses,[1] or dirty brown nodules; when bright it is paler in tint than pyrite, though this is not a constant character. It occurs frequently in many sedimentary rocks in the form of very minute particles, or sometimes in irregular layers; but being difficult to distinguish from pyrite, it is often supposed to be somewhat rarer than the latter. It oxidises more readily than pyrite on exposure, a whitish "scum" of ferrous sulphate being formed. This may be washed out of the clay by rain, or may be disseminated through it, and later be converted into red ferric oxide. Double sulphides of iron and copper occur also in some clays.

In many burned clays, iron sulphide may be detected, after firing, as minute

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[1] Stokes has noticed that much of the fibrous mineral usually termed marcasite is really pyrite.

black spots, which under the microscope have a semi-molten appearance. No matter how finely the nodules may be ground, they never appear to become converted into red ferric oxide, but, on heating, half the sulphur is expelled at 400° C. to 600° C., and the remainder at a higher temperature. If the material is heated rapidly, and with insufficient air during the second stage, the ferrous oxide produced combines with some of the silica present and forms a bluish-black slag.[1] This is of such a nature that it cannot be oxidised under the conditions obtaining in commercial furnaces, and it is, therefore, necessary when firing clays containing much pyrite to heat very slowly, and with an ample supply of air between 600° C. and 1000° C., or the goods will be marred by irregular blackening of the surface or interior.

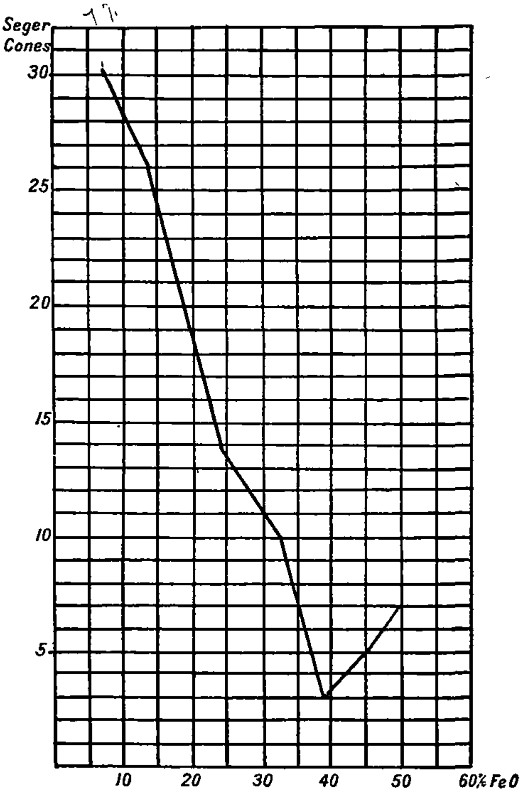

FIG. 11.—Effect of ferrous oxide on fireclay.

The odour of burning sulphur so often noticed in brickyards on the Coal Measures is largely due to the pyrite and marcasite in the clay and coal.

The effect of iron compounds on clays containing them is chiefly connected with the colour of the fired articles. If added to a refractory clay, iron compounds lower its fusing-point (fig. 11). They do not appear to diminish the

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[1] As ferrous compounds form more fusible silicates than ferric compounds, A. Gutensohn, in 1911, patented the addition of 1 per cent. of manganese peroxide to clays in order to oxidise the iron and thereby increase the refractoriness of the clay. This suggestion is of doubtful value.

plasticity of a clay, and they increase its cohesion after firing, as they act as mild fluxes.

In the case of pyrite, mundic, and marcasite (all sulphides), the damage they do is not simply dependent on the proportion in which they are present, but upon their peculiar ability to form ugly blotches of grey or black slag even after being finely ground. These blotches may entirely ruin the appearance of firebricks and other refractory articles even when the total percentage of iron present is extremely small. Hence, every effort must be made to keep the proportion of iron compounds as low as possible, and to remove whatever can be taken out previous to, or during, the grinding. That is, fortunately, not very difficult with most fireclays, as the greater part of the iron is present in the form of small nodules (pebbles or " kidneys "), which are easily recognised. If the large lumps of clay received from the pit are broken carefully, with sharp, rapid blows of a hammer, the clay will split without breaking the nodules, and they can then be cut out of the clay so completely that the small amount of pyrite left can do little harm.[1]

Ferrous and *ferric silicates* occur naturally as minerals, but none of them are important to manufacturers of firebricks. They are chiefly of interest because similar compounds are formed artificially when iron compounds are heated with silica or clay in burning firebricks, etc.

Nontronite ($Fe_2O_3.2SiO_2.2H_2O$) is particularly interesting, as it corresponds precisely to kaolinite, and on heating to redness is decomposed into free iron oxide, silica, and water.

Glauconite is an amorphous, granular, or earthy, hydrated potassic ferric silicate, alumina, magnesia, and lime being often present, as its composition is very variable. It is green in colour, and occurs extensively in marls from the chalk, chloritic marls, and particularly in the Greensands. It tends to give raw clay a greenish colour, which becomes reddish on burning, and aids vitrification, as it is readily fusible. It is, therefore, useful in some clays, but disadvantageous in those which are required to burn to a light-coloured refractory body.

A dark-coloured ferrous silicate of uncertain composition[2] is the chief colouring matter of the dark slag spots in firebricks, and is due to the ferrous sulphide, produced by heating pyrites, combining with the clay when heated in a reducing atmosphere or without sufficient air. It is extraordinarily difficult to completely oxidise the iron present in clays in the form of pyrites, and even when unusual precautions are taken some black slag spots of ferrous silicate will be formed.

Good fireclays should not contain more than 1½ per cent. of iron compounds, though a few of them contain over 3 per cent.

The effect of heat on all iron compounds which occur in clay is to decompose them. Under the usual conditions of industrial heating the products formed are ferric oxide (red), magnetite (black), and ferrous oxide (black). The two latter are very objectionable on account of their ready combination with the clay and silica, forming easily fusible compounds. Hence, it is necessary to exercise great care in selecting clays which contain a minimum of iron compounds. Many attempts have been made to remove the iron compounds from fireclays, but none of them are sufficiently cheap to be practicable under present conditions. (See " Purifying Clays.")

It is generally understood that the red ferric oxide is almost infusible, and

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[1] In most fireclays, some of the particles of iron sulphide are too small to be removed in this manner.

[2] It is often regarded as *fayalite*, $2FeO.SiO_2$.

this is true so long as it is not heated under conditions which affect its composition. Unfortunately, under the ordinary conditions of heating, this oxide is either reduced to magnetite or to ferrous oxide, so that, no matter what may be the particular compound of iron present, it is equally injurious to the refractoriness of the clay under the conditions in which the clay may at some time or other be heated.

Generally speaking, if the iron compounds are heated under exclusively oxidising conditions, their effect on the fusibility of the clay will be very slight. If, on the contrary, there is any reducing medium present, the iron compounds will be correspondingly reduced and will act as powerful fluxes. It is almost impossible to obtain completely oxidising conditions in industrial furnaces, so that the iron compounds in burned clays are in all stages of oxidation and reduction, and may rapidly change from one to the other during the heating or cooling of the furnace.

Lime compounds[1] are extremely widely distributed, and scarcely any clays are quite free from them. The refractory clays contain only 2 per cent. or even less, but some alluvial clays and marls contain as much as 45 per cent. of calcium carbonate,

In clays, lime compounds occur in a variety of different forms, of which the most important are calcium carbonate (calcite, aragonite, chalk, and limestone), gypsum, selenite, and other forms of calcium sulphate, as a phosphate, oligoclase-, and anorthite-felspars, and other silicates.

In commercially useful fireclays the total proportion of lime is so small that it is difficult to ascertain the form in which the lime occurs in these clays. Some of it is unquestionably combined directly with the clay.

Calcium carbonate ($CaCO_3$) is a compound of lime and carbon dioxide, which on being heated loses the latter constituent and forms *lime*. On exposure to moisture the lime becomes hydrated or "slaked," and in contact with carbon dioxide the carbonate is again formed. The calcium carbonate in the clay may be derived from the decomposition and pulverisation of limestone or chalk, or it may be deposited by water holding bicarbonate of lime in solution.

Some fireclays contain a few minute crystals of calcium carbonate (*aragonite*—$CaCO_3$) and of calcium sulphate (*selenite*—$CaSO_4 2H_2O$), but the proportion present is invariably small.

Calcium sulphate occurs in association with some fireclays in the form of gypsum ($CaSO_4 2H_2O$), the lath-like crystals of which may easily be recognised. On heating to a temperature above 1005° C., this substance dissociates, sulphur trioxide gas being evolved and lime left. Consequently, the effect of calcium sulphate in clay is similar to that of lime, except that the sulphur in it may cause additional trouble. It does little harm if it is evolved slowly in the form of sulphur trioxide, as is normally the case at 1005° C., but above this temperature (1050° C. to 1100° C.) it is evolved very rapidly, and may cause "blowing." A very peculiar fact about some clays containing gypsum is their retention of plasticity at a temperature much higher than under ordinary conditions.

The *calcium phosphate* which occurs in minute proportions in some fireclays appears to be derived from fossilised animal excreta, corresponding to the *coprolites* found in the Greensand clays. The ordinary mineral form of calcium phosphate—*apatite*—occurs in very small proportions in some fireclays. In most cases, the proportion of calcium phosphate in refractory clays is too

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[1] Strictly, these should be termed calcium compounds, but the term employed in the text is that commonly used by clayworkers.

small to have any serious effect on the quality of the goods; any large pieces which may occur are usually removed by hand.

Calcium silicates and *alumino-silicates* occur as natural minerals in some fireclays, and are also formed during the burning of impure clays containing lime compounds. Four compounds of silica and lime are known, viz.: *tricalcium silicate* ($3CaO.SiO_2$); *calcium orthosilicate* ($2CaO.SiO_2$); *tricalcium disilicate* ($3CaO.2SiO_2$); and *calcium metasilicate* ($CaO.SiO_2$).

Tricalcium silicate and *tricalcium disilicate* do not appear to occur in clays, as they are easily decomposed in the presence of water, forming the ortho- and meta-silicates and free lime. *Calcium metasilicate* occurs in nature as wollastonite, but the artificially prepared material exists in two modifications: α, stable between the melting-point and 1512° C.; β, stable at all temperatures below the transition-point. According to Boudouard, the metasilicate is the most fusible compound of lime and silica.

Calcium orthosilicate exists in three modifications: α, which is stable only above 1410° C., with a specific gravity of 3·27 and crystallising in monoclinic prisms with a hardness of 5 to 6 on Mohs' scale; β, stable between 1410° C. and 675° C., forming orthorhombic crystals with a specific gravity of 3·28; and γ, stable below 675° C., with a specific gravity of 2·97. When a molten mass containing calcium orthosilicate is cooled, an increase in the volume of the orthosilicate occurs during the transition, and accounts for the disintegration of the orthosilicate on cooling. When calcium orthosilicate is heated strongly in the presence of sufficient silica, calcium metasilicate is formed. For further information see Tables XXII., XXIII., and XXXV. to XXXVII.

Calcium aluminates may exist in small proportions in some burned clays; the two most important being $5CaO.3Al_2O_3$, which melts at 1386° C., and $3CaO.Al_2O_3$, which is formed at about 1530° C. Two other calcium aluminates, prepared artificially by G. A. Rankin and F. E. Wright, viz., $CaO.Al_2O_3$ and $3CaO.5Al_2O_3$, have not been found in either raw or burned clays. The *calcium alumino-silicates* which occur in clays are chiefly lime felspars, but epidote, zoisite, and zeolites are also present in some clays.

The effect of a small proportion of lime compounds on the fireclays in which they occur is to lower the refractoriness of the latter. If lime compounds are purposely added to a clay they increase the fusibility to such an extent as to remove the mixture from the category of refractory clays. The effect is the same no matter what compound of lime is added, or is naturally present in the clay. If calcium carbonate is present, it loses carbon dioxide at a temperature of about 700° C., whilst any calcium sulphate which may be present is decomposed at about 1005° C. In both cases the residual product is free lime in a condition ready to attack either the clay or free silica in its immediate vicinity. J. Cobb has found on heating lime and silica, calcium orthosilicate ($2CaO.SiO_2$) is formed, unless there is a very large excess of silica present when the metasilicate is produced. The temperature at which these substances are formed is in all cases below that of the melting-points of lime and silica [1] or that of the eutectic, and is quite complete at 800° to 1400° C., so that no fusion need occur in the formation of the calcium silicate. Nor is there any necessity for the materials to attain the higher temperature, as a prolonged heating at a lower temperature is just as effective in producing the silicate.

When free lime and free alumina are present in the clay, the temperature at which interaction takes place is about 850°C. to 900° C., and is fairly constant whatever the proportions of lime and alumina present. J. Cobb has found that, with equal proportions of lime and alumina, the reaction is very rapid

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[1] Lime melts at 2570° C. and silica at 1625° C.

at 1100° C. and is practically complete at 1300° C., the compound formed being $CaO.2Al_2O_3$, which is soluble in cold hydrochloric acid. Above 1100° C. an insoluble compound richer in alumina is formed, and the amount of soluble aluminate correspondingly diminished.

The reactions of lime with either silica or alumina alone are relatively simple, but when both are present simultaneously, as in clays, the product is much more complex, and the nature of the reactions is by no means well known. It appears to be fairly certain, however, that either one or both of the following may occur:—

(i) The lime and silica may combine to form calcium silicates, and the lime and alumina to form calcium aluminates as previously described; or,

(ii) One or more ternary compounds or alumino-silicates may be produced.

The extent to which these reactions will occur depends chiefly on the relative quantities of each of the constituents present, the size of the particles, the temperature to which the mixture is heated, and the duration of the heating. If clays are complex stable alumino-silicic acids, as suggested by Asch, it would seem natural that the principal compounds formed would be alumino-silicates, and various researches on the constitution of Portland cement seem to indicate this, though, if complete fusion takes place in the presence of an excess of lime, these complexes are sometimes decomposed into simple silicates and aluminates. J. W. Cobb's experiments seem to show that the soluble compounds first formed are simple aluminates and silicates, whilst the insoluble ones which are produced on further heating are ternary compounds, *i.e.* alumino-silicates. G. A. Rankin, on the other hand, suggests that $5CaO.3Al_2O_3$ is first formed, and is followed by $2CaO.SiO_2$, and that these compounds then absorb lime slowly, and at 1335° C. the fluid mass consists of a mixture of $2CaO.SiO_2$, $5CaO.3Al_2O_3$, and $3CaO.Al_2O_3$, which at a higher temperature forms $3CaO.Al_2O_3$ and $3CaO.SiO_2$, the latter finally dissociating into free lime and $2CaO.SiO_2$. If, on the other hand, clays decompose on heating to 600° C. to 1000° C. into free silica and free alumina, it would be reasonable to suppose that simple lime compounds would be formed, though some secondary alumino-silicates might be produced by the interaction of the simpler compounds. Unfortunately, the relative proportions of the various products cannot be determined satisfactorily by any practical methods yet devised, because crystallisation and partial fusion occurs simultaneously, and the same results are not obtained with the fused materials as when no fusion has occurred. Even an elaborate microscopic examination of the heated material does not help to any great extent in elucidating the problem, as the proportion of silicate, aluminate, and alumino-silicate formed in burned clays is seldom sufficiently large to justify definite conclusions being drawn, and the results of the examination of Portland cement clinker, and of fused mixtures of lime, silica, and alumina cooled under various conditions, do not necessarily apply to heated fireclays. Moreover, the evidence obtained by different investigators is, at present, so complex and so often contradictory that no definite and satisfactory conclusion can be drawn from it.

The effect of lime on clay is shown in the following results obtained by Rieke.[1] Tables XIII. to XV. should be studied in conjunction with fig. 12, in which the same results are represented graphically.

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[1] Rieke (*Sprechsaal*, 1907, Nos. 45, 46) used a mixture of Zettlitz kaolin, lime, and quartz in molecular proportions. The results are calculated on the heated material; this explains the absence of H_2O in the formulæ.

TABLE XIII.—FUSING-POINTS OF KAOLIN-LIME MIXTURES.

Mol. CaO to 1 Mol. $Al_2O_3.2SiO_2$.	Per cent. Al_2O_3.	Per cent. SiO_2.	Per cent. CaO.	Fusing-Point (Seger Cones).	Mol. CaO to 1 Mol. $Al_2O_3.2SiO_2$.	Per cent. Al_2O_3	Per cent. SiO_2.	Per cent. CaO.	Fusing-Point (Seger Cones).
0·0	45·8	54·2	..	35	4·0	22·9	27·0	50·1	19
0·1	44·7	52·9	2·4	34	4·1	22·6	26·7	50·7	18–19
0·2	43·6	51·6	4·8	31	4·3	22·0	26·1	51·9	18
0·25	43·1	51·0	5·9	28–29	4·5	21·5	25·4	53·1	17–18
0·3	42·6	50·4	7·0	26–27	4·6	21·3	25·1	53·6	17
0·4	41·7	49·2	9·1	18	4·8	20·8	24·6	54·6	16–17
0·45	41·2	48·7	10·1	15	5·0	20·3	24·0	55·7	16
0·5	40·7	48·1	11·2	15–16	5·1	20·1	23·7	56·2	15–16
0·55	40·3	47·4	12·4	16	5·3	19·7	23·2	57·1	15
0·75	38·6	45·6	15·8	17	5·5	19·2	22·8	58·0	14–15
0·8	38·2	45·1	16·7	17	5·75	18·7	22·2	59·1	13–14
0·9	37·4	44·2	18·4	18	5·9	18·5	21·8	59·7	13
1·0	36·6	43·3	20·1	18–19	6·0	18·3	21·6	60·1	14
1·1	35·9	42·5	21·6	17	6·25	17·8	21·1	61·1	15–16
1·25	34·9	41·2	23·9	15	6·5	17·4	20·6	62·0	16–17
1·5	33·3	39·3	27·4	13	7·0	16·6	19·6	63·8	18
1·75	31·8	37·7	30·5	9	7·5	15·9	18·8	65·3	19
1·9	31·0	36·7	32·3	7–8	7·75	15·5	18·4	66·1	19–20
2·0	30·5	36·1	33·4	7	8·0	15·2	18·0	66·8	20
2·1	30·0	35·5	34·5	7	8·25	14·9	17·6	67·5	20
2·25	29·3	34·6	36·1	8	8·5	14·6	17·3	68·1	20–26
2·5	28·1	33·3	38·6	9	8·75	14·3	17·0	68·7	26
3·0	26·1	30·9	43·0	11–12	9·0	14·1	16·6	69·3	26
3·1	25·8	30·4	43·8	12	9·25	13·8	16·3	69·9	26–27
3·5	24·4	28·8	46·8	15	9·5	13·5	16·0	70·5	27
3·75	23·6	27·9	48·5	17	10·0	13·1	15·4	71·5	27
3·9	23·1	27·4	49·5	18–19	12·0	11·4	13·5	75·1	27

TABLE XIV.—FUSING-POINTS OF KAOLIN-LIME MIXTURES.

Mol. CaO to 1 Mol. $Al_2O_3.3SiO_2$.	Per cent. Al_2O_3.	Per cent. SiO_2.	Per cent. CaO.	Fusing-Point (Seger Cones).	Mol. CaO to 1 Mol. $Al_2O_3.3SiO_2$.	Per cent. Al_2O_3.	Per cent. SiO_2.	Per cent. CaO.	Fusing-Point (Seger Cones).
0·0	36·0	64·0	..	33	2·1	25·5	45·2	29·3	9–10
0·1	35·4	62·7	1·9	31	2·25	24·9	44·3	30·8	9
0·2	34·7	61·5	3·8	30	2·5	24·1	42·8	33·1	6–7
0·25	34·4	60·9	4·7	29	3·0	22·6	40·2	37·2	6–7
0·3	34·0	60·4	5·6	28	3·5	21·3	37·8	40·9	7
0·4	33·4	59·3	7·3	19	4·0	20·1	35·7	44·2	7
0·45	33·1	58·7	8·2	16–17	4·5	19·1	33·8	47·1	7
0·5	32·8	58·2	9·0	14–15	5·0	18·1	32·2	49·7	6
0·55	32·5	57·7	9·8	15	5·5	17·3	30·6	52·1	15
0·75	31·4	55·7	12·9	15	5·75	16·9	29·9	53·2	17
0·8	31·1	55·2	13·7	15	6·0	16·5	29·3	54·2	19–20
0·9	30·6	54·3	15·1	15–16	6·25	16·1	28·6	55·3	19
1·0	30·1	53·4	16·5	15–16	6·5	15·8	28·0	56·2	19
1·1	29·6	62 5	17·9	15	7·0	15·1	26·8	58·1	19
1·25	28·9	51·3	19·8	13	7·5	14·5	25·8	59·7	20
1·5	27·8	49·3	22·9	11–12	8·0	14·0	24·8	61·2	20–26
1·75	26·8	47·5	25·7	9	9·0	13·0	23·0	64·0	27–28
1·9	26·2	46·5	27·3	9–10	10·0	12·1	21·5	66·4	29
2·0	25·9	45·8	28·3	10	12·0	10·7	19·0	70 3	31–32

TABLE XV.—FUSING-POINTS OF KAOLIN-LIME MIXTURES.

Mol. CaO to 1 Mol. $Al_2O_3.4SiO_2$.	Per cent. Al_2O_3.	Per cent. SiO_2.	Per cent. CaO.	Fusing Point (Seger Cones).	Mol. CaO to 1 Mol. $Al_2O_3.4SiO_2$.	Per cent. Al_2O_3.	Per cent. SiO_2	Per cent. CaO.	Fusing-Point (Seger Cones).
0·0	29·7	70·3	0·0	32	3	20·0	47·1	32·9	5
0·25	28·6	67·5	3·9	27	4	18·0	42·5	39·5	6
0·5	27·5	64·9	7·6	12	5	16·4	38·7	44·9	7
1	25·6	60·4	14·0	10	6	15·0	35·6	49·4	7-8
1·5	23·9	56·4	19·7	8	8	12·9	30·5	56·6	17-18
2	22·4	53·0	24·6	5–6	10	11·3	26·7	62·0	26
2·5	21·1	49·9	29·0	6					

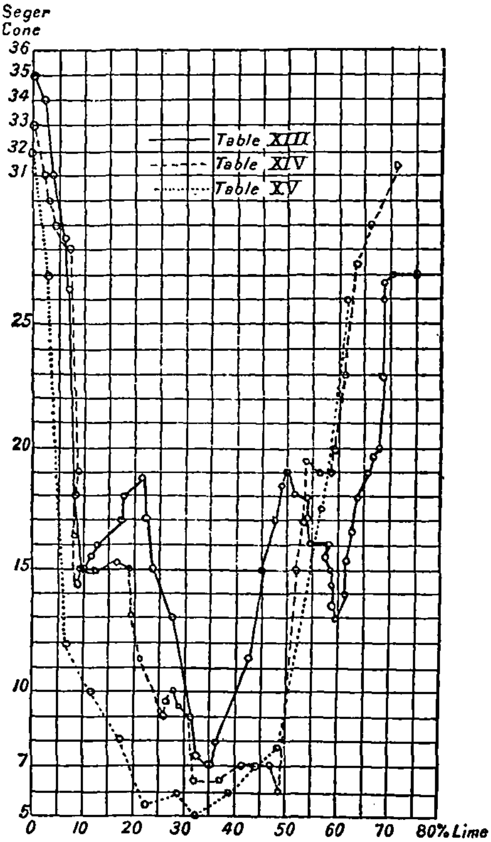

FIG. 12.—Effect of lime on kaolin and on mixtures of kaolin and silica.

When these results are represented graphically, as in fig. 12, the effect of the free silica (as shown by the dotted curves) is very marked. If the results are expressed in the form of a triaxial diagram (fig. 3A), it is found that th eutectic axis and lines of equi-refractoriness are similar to those for magnesia (fig. 14), but the eutectics have lower melting-points.

The action of lime may be altered by the presence of other fluxes in the clay. When alkalies are present simultaneously with lime (as is usually the case), they reduce the temperature at which the glassy material is formed, as sodium and potassium silicates and alumino-silicates are formed at a lower temperature and fuse more readily than the corresponding lime compounds. Moreover, when any fused matter has been formed, it acts as a solvent of lime, silica, alumina, and clay, and thereby facilitates the progress of the reaction between these materials.

The effect of lime on the colour of burned clays containing iron compounds has already been mentioned. When a clay containing lime and ferric oxide is heated sufficiently, either *calcium metaferrate*, $CaO.Fe_2O_3$ (M.P. 1205° C.), or *calcium orthoferrate*, $2CaO.Fe_2O_3$ (M.P. 1400° C.), may be formed. According to R. B. Sosman and H. E. Merwin, both these substances dissociate at their melting-points, the latter giving crystals of a blue-black colour with a yellowish-brown tinge by transmitted light, and the former giving long black needle-shaped crystals. The proportion of calcium ferrate in any fireclay is so small that it may usually be neglected.

In all cases, the fused or glassy material formed by the reaction of lime compounds on the other constituents of fireclays rapidly flows through the porous mass of clay, filling the pores and eventually, if sufficient glass is present, causing the mass to lose its shape. The smaller the particles and the higher the temperature, the more violent will be the action of the lime on the clay. The extent to which this closing of the pores, or vitrification, occurs can be determined by measuring the porosity of the material after it has been heated at different temperatures, the porosity decreasing with the increased fluxing action of the lime.

Barium compounds sometimes exist in clay in notable proportions, and in analyses are generally included with the lime. The principal forms in which barium compounds occur are *barium carbonate* (*witherite*, $BaCO_3$), which is never present in more than very small and variable proportions, and *barium sulphate* (*barytes*, $BaSO_4$), which may occur either as crystals, or more frequently as a cementing agent uniting the particles of clay or shale, as at Seaton, Northumberland.

Barium compounds act so similarly to the corresponding lime compounds that they need not be described separately.

Magnesium compounds also occur in similar proportions to lime compounds in clays. They are derived in a similar manner from the destruction of magnesian rocks, and in many ways act like the corresponding compounds of lime. The chief form in which magnesium enters into commercial clays is as *magnesite* (*magnesium carbonate*, $MgCO_3$), but a very small proportion of *magnesium sulphate* ($MgSO_4.7H_2O$, M.pt. 160° C.) may also, occasionally, be present. As the latter is readily soluble in water, it passes to the outside of the bricks or other articles during the drying, and there forms a light crystalline fur or "scum," which may easily be rubbed off.

Magnesium carbonate occurs in some clays as fibrous crystals, but in fireclays it is in so finely powdered a condition as to be unrecognisable. The proportion in British fireclays is never large, 3 per cent. apparently being the maximum, even in the lowest grades of fireclay. On heating, it forms *magnesia* (MgO)—a material very similar to lime, but much slower in its action; the melting-point of magnesia is 2800° C.

The action of magnesia on clay may be judged from figs. 13 and 14, the former showing graphically the results obtained by Rieke,[1] and given in a somewhat different form in Table XVI. It will be seen that up to 47·4 per cent. of magnesia lowers the melting-point of a clay in proportion to the amount of magnesia added. With a greater proportion of magnesia, however, chemical combination takes place, and the refractoriness gradually increases with the increasing proportions of magnesia until, with 64 per cent. of magnesite, the softening point is Cone 29 (1650° C.) as compared with Cone 34 (1750° C.) for the kaolin alone.

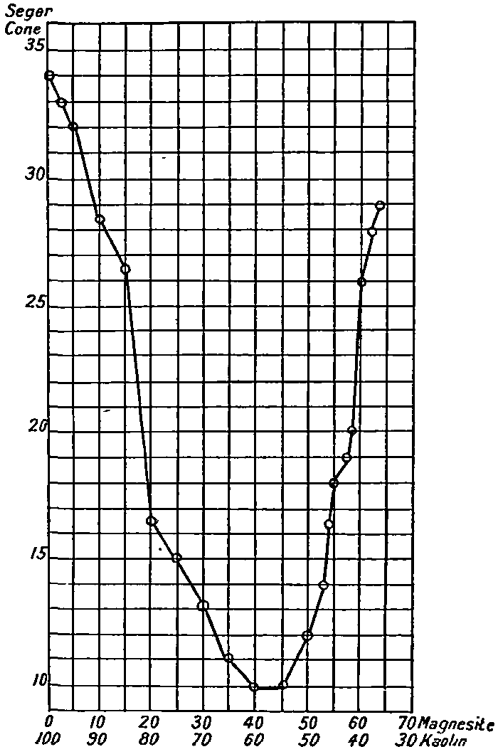

FIG. 13.—Refractoriness of mixtures of magnesite and kaolin.

The most fusible mixture of magnesia and china clay has, according to Rieke,[1] the formula $5MgO.Al_2O_3.2SiO_2$, and is made by mixing 10 parts of the clay with 9 parts of magnesia. This eutectic fuses at Seger Cone 10 (1300° C.). Rieke's figures are not accepted by some other investigators, for G. A. Rankin and H. E. Merwin [2] state that four compounds may be formed by heating magnesia and clay, viz.: *forsterite*, $2MgO.SiO_2$; *clinoenstatite*, $MgO.SiO_2$; *spinel*, $MgO.Al_2O_3$; and *cordierite*, $2MgO.2Al_2O_3.5SiO_2$. Of these compounds, clinoenstatite and cordierite dissociate at the melting-point of the mixture, but cordierite may crystallise when the molten material is cooled below 950° C.; at higher temperature it is transformed into a stable α form, which dissociates on melting. Again,

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[1] *Sprechsaal*, 1907, No. 17.

[2] *Journ. Amer. Chem. Soc.*, 1918, p. 301.

according to N. L. Bowen[1] several eutectics are formed at various temperatures, one of the most important being that of magnesia (periclase) with forsterite, which melts at 1850° C., *i.e.* 40° C. below the melting-point of forsterite. Bowen has found no eutectic to exist between forsterite and clinoenstatite, but states that the latter forms a eutectic with silica (cristobalite) by the action of heat on clay at 1543° C.

TABLE XVI.—FUSING-POINTS OF KAOLIN-MAGNESITE MIXTURES.

Magnesite. Per cent.	To 100 Parts Kaolin are added	Fusing-Point (Seger Cones).	Magnesite. Per cent.	To 100 Parts Kaolin are added	Fusing-Point (Seger Cones).
1	1 part magnesite	34	45	81·8 part magnesite	10
3	3·1 „ „	33	50	100·0 „ „	12
5	5·3 „ „	32	52	108·3 „ „	14
10	11·1 „ „	28–29	54	117·3 „ „	16–17
15	17·6 „ „	26–27	55	122·2 „ „	18
20	25·0 „ „	16–17	56	127·3 „ „	19
25	33·3 „ „	15	58	138·1 „ „	20
30	42·9 „ „	13	60	150·0 „ „	26
35	53·8 „ „	11	62	163·2 „ „	28
40	66·7 „ „	10	64	177·8 „ „	29

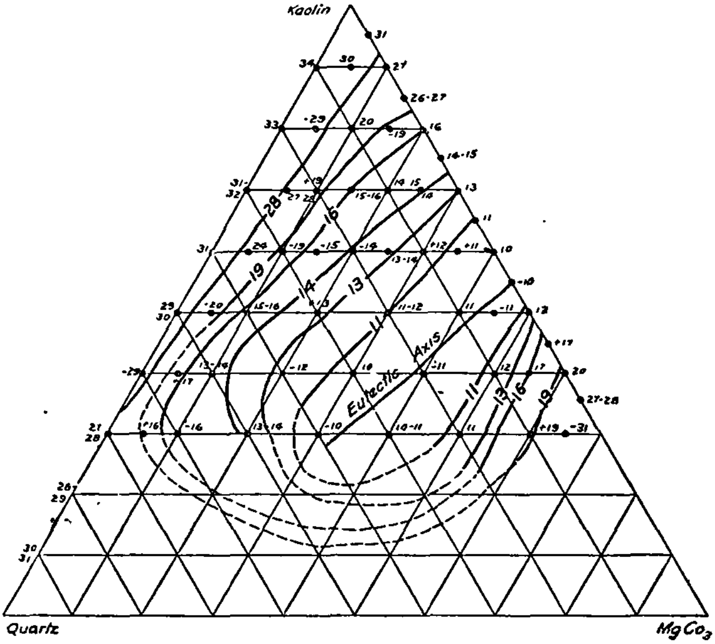

FIG. 14.—Refractoriness of mixtures of magnesite, kaolin, and quartz.

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[1] *Amer. Journ. Sci.*, 1914, iv. 38, 307.

Rieke found that when free silica is also present, several important changes occur. These are shown in Table XVII. and graphically in fig. 14.

It is particularly interesting to compare fig. 13 with fig. 14, which is due to Purdy, who calculated it from the figures shown in Table XVII.

TABLE XVII.—FUSING-POINTS OF CLAY-QUARTZ-MAGNESITE MIXTURES.

To 100 Parts of Kaolin are added		Fusing-Point (Seger Cones).	To 100 Parts of Kaolin are added		Fusing-Point (Seger Cones).
Quartz.	Magnesite.		Quartz.	Magnesite.	
133·3	100	10	200	33·3	16
75	75	10	216·7	16·7	16
100	133·3	10–11	12·5	137·5	17
50	100	11	137·5	12·5	17
10	90	11	50	16·7	19
66·7	166·7	11	6·2	18·8	19
20	80	11	28·6	14·2	19
8·3	58·3	11	33·3	200	19
40	60	11–12	90	10	20
100	50	12	12·5	12·5	20
25	125	12	58·3	8·3	20–26
16·7	50	12	233·3	..	27–28
60	40	13	35·7	7·1	27–28
25	41·7	13–14	18·8	6·2	29
166·7	66·7	13–14	150	..	29
125	25	13–14	100	..	29–30
33·3	33·3	14	5·5	5·5	30
7·1	35·7	14	16·7	216·7	31
14·2	28·6	14–15	66·7	..	31
41·7	25	15	42·9	..	31–32
21·4	21·4	15–16	25	..	33
80	20	15–16	11	..	34

This triaxial diagram shows a series of lines of equi-refractoriness about an axis (*cf.* the line A B in fig. 3A). Such triaxial diagrams have the advantage over graphs, such as fig. 13, inasmuch as they enable the effect of the alumina and silica in the clay to be observed separately in a manner impossible in a simple graph (fig. 13). The triaxial diagrams also show that, in some instances, several eutectics are possible—a fact which is not so clearly ascertainable from a simple graph.

Magnesia and magnesite increase the shrinkage of a clay, but articles made from such mixtures retain their shape in a remarkable manner when heated, whereas in mixtures of clay and lime or chalk the range of vitrification is extremely short, and loss of shape occurs at a very short interval after the commencement of the fusion of the calcium silicate, etc. This delay in the loss of shape, due to a long range of vitrification, is one of the great advantages gained in using magnesia or magnesite as a flux, and it is very useful in some branches of clayworking. It appears to be due to the molten magnesia complex being highly viscous and "tacky," whilst the molten lime complex forms a thin and very mobile fluid which readily attacks the surrounding particles.

When magnesia is present in small proportions, it slightly increases the density of a fireclay at low temperatures, but has the disadvantage of making clays extremely "short"—even 5 per cent. of magnesia being serious in this respect—and so causing much trouble in moulding.

Alkalies is a term including all compounds of potash and soda which occur in clay, as these act so similarly as to render their differentiation unnecessary. *Ammonium salts* are also present in some raw clays, but their proportion is seldom determined; they may slightly increase the fusibility of a clay or modify its plasticity, but their effect is usually negligible. They are volatilised on heating the clay.

The fixed alkalies (potash and soda compounds), on the contrary, remain in the clay after firing, and are the most powerful fluxes known. At the high temperatures reached in some kilns, a partial volatilisation of alkalies occurs, the material then becoming slightly more refractory. This fact is one of the reasons for the use of grog for retorts and firebricks.

Although reports of analysis usually state the percentage of alkalies in terms of potash (K_2O) and soda (Na_2O), these oxides seldom exist in these forms in clays. The most usual forms are *alkali-alumino-silicates*, such as felspar, mica, Cornish stone, Greensand (*glauconite* contains potash), and hornblende, but only the first three are really important in this respect. All these minerals are practically insoluble in water, and they form a convenient means of applying fluxing materials to clays which are not sufficiently vitrifiable, the felspars and Cornish stone being much used for this purpose in pottery.

A small proportion of alkali and lime in a fireclay binds the particles together, producing a stronger mass than when the alkali is absent. Hence, the presence of very small proportions of alkalies and bases in firebricks may increase the strength and, therefore, the value. In larger proportions they are detrimental for the reasons given above. It is generally inadvisable for a good fireclay to contain more than 2 per cent. of potash and soda, but a few excellent fireclays contain as much as 5 per cent.

Occasionally clays contain soluble alkali salts, usually potassium and sodium sulphate, and sodium chloride (common salt) is not infrequent. Sulphates due to the oxidation of pyrite or marcasite may also be present. If the proportion of these *soluble salts* is small, the effect is a slight reduction in the refractoriness of the clay; but if larger, they tend to be drawn to the surface of the goods made from the clay and to form an unpleasant white scum or slight irregular glaze on the fired articles. This scum may usually be removed by rubbing the dried article prior to burning it.

The following soluble substances reduce the plasticity of a clay: ammonia, caustic soda, caustic potash, lime, sodium carbonate, potassium carbonate, borax, and water-glass. They do this by dispersing the colloidal portion of the clays,[1] but their action may be prevented by the addition of a quantity of weak acid sufficient to neutralise the alkali. The addition of these substances facilitates the manufacture of some articles by the "casting" process.

The effects of alkalies on clays containing them are, therefore (*a*) to increase the fusibility, (*b*) to produce a scum on the surface of the goods, and (*c*) to diminish the plasticity of the clay when it is made into a paste with water and so to facilitate casting.

It is by no means essential that the whole of the alkalies should be in a combined form, and Binns has shown that free alkali is present in small quantities in some clays; ordinarily, however, they exist in the form of

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[1] For a more detailed account see p. 117.

felspar, mica, or other silicates, which are described later in the present chapter.

It was at one time thought that the alkalies contained in clays were found exclusively in the state of impalpably powdered felspar, but Vogt has shown that this opinion is erroneous, and that they also exist in the form of finely divided mica. It is not a little curious that most British, American, and German experts consider that the alkalies occurring in the finest particles of clays are in the form of felspar, whilst the French experts maintain that they exist as mica. As a matter of fact they exist in some clays as felspar, in others as mica, and in others again in both forms, as may readily be found by careful investigation.

Felspar is the term applied to a group of alumino-silicates containing one or more alkaline or basic oxides—lime or magnesia—and are usually distinguished by the name of the predominant oxide, *e.g.* potash felspar, lime felspar, etc.

The principal potash felspar is *orthoclase*, which, when pure, contains about 16 per cent. of potash, 18 per cent. of alumina, and 65 per cent. of silica. This is the purest commercial felspar and the one most generally used by clayworkers, as it gives a better " ring " than ware made with either soda or lime felspars. When heated alone, pure orthoclase or potash felspar melts at a temperature just below 1200° C., according to Day and his associates, but the best commercial material, when heated in a large kiln under commercial conditions alongside Seger cones, fuses at the temperature at which Cone 9 bends over, which is equivalent to 1280° C. The difference is largely due to a little impurity in the felspar and to the time taken to melt a comparatively large piece; small grains melt more rapidly at an apparently lower temperature. It is, however, very difficult to tell exactly at what temperature it melts on account of its long softening range, which makes accurate estimations on a large scale almost impossible. At a temperature of about 1120° C., potash felspar expands very slightly, and its specific gravity is reduced by 0·2 per cent. When a mixture of potash felspar and quartz is heated, it does not commence to vitrify appreciably below 1200° C., but when a moderate amount of fusion has occurred, the whole mass vitrifies very rapidly at this temperature. A mixture of potash felspar and kaolin softens at 1100° C., but shows no eutectic, the refractoriness rising steadily (according to Simonis) with each addition of clay to the felspar.

The heated mixtures become slightly denser at Cone 1*a* (1100° C.), and notably so at higher temperatures. The action of the felspar increases with the fineness of the grinding, and if both felspar and clay are ground to flour, a fully impervious mixture can be produced at Cone 2*a* (1120° C.).

The effect of felspar on the contraction and porosity of china clay on heating in a china biscuit oven (Cone 9) is shown in Table XVIII., prepared by A. Heath.

The effect of heat on a mixture of Zettlitz kaolin, orthoclase felspar, and quartz (according to H. Simonis) is shown in Table II.

One beneficial feature of the fluxing action of felspar is that it is quite slow, and so it does not permit premature loss of shape to occur so rapidly as sometimes occurs with other fluxes. Felspar may be considered, therefore, as a safe flux, and a small amount of it in a clay is of less consequence than an equal quantity of any other flux likely to occur as an impurity in clay.

TABLE XVIII.—CONTRACTION AND POROSITY OF CHINA-CLAY-FELSPAR MIXTURES.

Trial No.	Felspar.	China Clay.	Contraction.	Porosity.	Trial No.	Felspar.	China Clay.	Contraction.	Porosity.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.		Per Cent.	Per Cent.	Per Cent.	Per Cent.
1	100·0	..	6·85	0·265	22	47·5	52·5	11·625	0·78
2	97·5	2·5	6·75	0·293	23	45·0	55·0	11·25	0·368
3	95·0	5·0	6·625	0·181	24	42·5	57·5	12·375	0·315
4	92·5	7·5	6·625	0·281	25	40·0	60·0	13·00	0·458
5	90·0	10·0	7·50	0·368	26	37·5	62·5	12·75	0·39
6	87·5	12·5	8·375	0·409	27	35·0	65·0	13·00	0·26
7	85·0	15·0	8·00	0·404	28	32·5	67·5	13·00	0·283
8	82·5	17·5	8·25	0·300	29	30·0	70·0	12·75	0·344
9	80·0	20·0	9·00	0·263	30	27·5	72·5	13·125	0·433
10	77·5	22·5	7·625	0·176	31	25·0	75·0	13·50	0·463
11	75·0	25·0	8·25	0·264	32	22·5	77·5	13·50	2·081
12	72·5	27·5	8·25	0·267	33	20·0	80·0	13·50	4·522
13	70·0	30·0	8·375	0·125	34	17·5	82·5	13·25	6·003
14	67·5	32·5	8·00	0·370	35	15·0	85·0	13·00	9·536
15	65·0	35·0	8·50	0·341	36	12·5	87·5	12·25	10·386
16	62·5	37·5	8·75	0·308	37	10·0	90·0	11·65	11·857
17	60·0	40·0	8·75	0·290	38	7·5	92·5	11·00	14·871
18	57·5	42·5	8·75	0·310	39	5·0	95·0	10·75	17·132
19	55·0	45·0	9·75	0·287	40	2·5	97·5	10·50	19·39
20	52·5	47·5	10·25	0·416	41	..	100·0	8·75	22·50
21	50·0	50·0	11·125	0·356					

The effect of heat on a mixture of felspar (orthoclase) and silica (quartz) is also shown in the following table, due to J. A. Douglas :—

TABLE XIX.—FUSING-POINTS OF ORTHOCLASE-QUARTZ MIXTURES.

Mixture.	Formula.	Percentage Composition.			Fusing-Point.
Orthoclase .	$K_2O.Al_2O_3.6SiO_2$	$16{\cdot}9K_2O$	$18{\cdot}3Al_2O_3$	$64{\cdot}8SiO_2$	1220° C.
2 orthoclase : 3 quartz .	$1K_2O.1Al_2O_3.7{\cdot}5SiO_2$	$14{\cdot}5K_2O$	$15{\cdot}7Al_2O_3$	$69{\cdot}8SiO_2$	1265° C.
1 orthoclase : 2 quartz .	$1K_2O.1Al_2O_3.8SiO_2$	$13{\cdot}8K_2O$	$15{\cdot}0Al_2O_3$	$71{\cdot}2SiO_2$	1285° C.
1 orthoclase : 3 quartz .	$1K_2O.1Al_2O_3.9SiO_2$	$12{\cdot}7K_2O$	$13{\cdot}8Al_2O_3$	$73{\cdot}5SiO_2$	1292° C.
1 orthoclase : 6 quartz .	$1K_2O.1Al_2O_3.12SiO_2$	$10{\cdot}2K_2O$	$11{\cdot}1Al_2O_3$	$78{\cdot}7SiO_2$	1317° C.

The soda and lime felspars form a series extending from pure soda felspar (albite) to pure calcium felspar (anorthite) ; the fusibility of various mixtures of felspars are shown in fig. 15 (drawn by R. C. Purdy), and in the following table, due to Day and his associates :—

TABLE XX.—FUSING-POINTS OF FELSPAR MIXTURES.

Felspar.	Formula.	Percentage Composition.	Fusing-Point.
			° C.
Albite . . .	$Na_2O.Al_2O_3.6SiO_2$	$11·8Na_2O$ CaO $19·4Al_2O_3$ $68·8SiO_2$	under 1200
Oligoclase andesine .	3 Albite+1 Anorthite= $\left\{\begin{matrix}0·6Na_2O\\0·4CaO\end{matrix}\right\}1Al_2O_3.4·4SiO_2$	$8·7Na_2O$ $5·2CaO$ $23·9Al_2O_3$ $62·2SiO_2$	1345
Andesine . . .	2 Albite+1 Anorthite= $\left\{\begin{matrix}0·5Na_2O\\0·5CaO\end{matrix}\right\}1Al_2O_3.4SiO_2$	$7·7Na_2O$ $6·9CaO$ $25·3Al_2O_3$ $60·1SiO_2$	1375
Andesine-labradorite	1 Albite+1 Anorthite= $\left\{\begin{matrix}0·33Na_2O\\0·66CaO\end{matrix}\right\}1Al_2O_3.3·33SiO_2$	$5·7Na_2O$ $10·3CaO$ $28·3Al_2O_3$ $60·1SiO_2$	1430
Labradorite . .	1 Albite+2 Anorthite= $\left\{\begin{matrix}0·2Na_2O\\0·8CaO\end{matrix}\right\}1Al_2O_3.2·8SiO_2$	$3·8Na_2O$ $13·7CaO$ $31·1Al_2O_3$ $51·4SiO_2$	1477
Bytownite .	1 Albite+5 Anorthite= $\left\{\begin{matrix}0·09Na_2O\\0·91CaO\end{matrix}\right\}1Al_2O_3.2·36SiO_2$	$1·9Na_2O$ $16·9CaO$ $33·9Al_2O_3$ $47·3SiO_2$	1516
Anorthite . .	$CaO.Al_2O_3.2SiO_2$	$20·1CaO$ $36·6Al_2O_3$ $43·3SiO_2$	1532

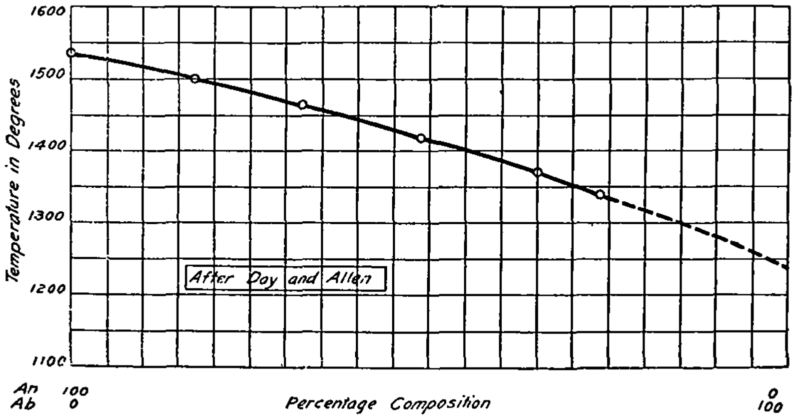

FIG. 15.—Refractoriness of mixtures of anorthite and albite felspars.

Mica is a term used to include a number of alumino-silicates. Muscovite or potash mica has a formula $K_2O.3Al_2O_3.6SiO_2$, corresponding to 12·3 per cent. potash, 40·2 per cent. alumina, and 47·5 per cent. silica. Rieke found its fusion-point corresponded to Seger Cone 13 (1395° C.).

Crude china clays, ball clays, and fireclays in the United Kingdom often contain a noteworthy proportion of mica but scarcely any felspar. The particular mica most frequently found in clays is muscovite. Biotite occurs more rarely, as it decomposes on exposure to the weather.

Where an intense whiteness is required in the burned clay, mica, especially biotite, is objectionable on account of the iron it contains.

The softening effect of mica on a refractory clay is seldom noticeable below 1200° C., though when unusually finely divided its action begins at a much lower temperature.

Mixtures of mica and clay show no eutectic (see fig. 3), but behave like mixtures of felspar and china clay. With alumina, muscovite forms an eutectic containing about 90 per cent. of mica and 10 per cent. of alumina (fig. 4), which, according to Rieke, melts at Seger Cone 12 (1375° C.).

The effect of mica on fireclay is similar to its action on china clay. It reduces the refractoriness of the clay, though not to the same extent as potash felspar. It also increases the kiln-shrinkage to a small extent, except where muscovite is in fairly large proportion, when a slight expansion occurs at about Cone 10 (1300° C.).

With quartz, mica forms a eutectic containing equal parts of each substance (fig. 5). This eutectic, according to Rieke, melts at Seger Cone 19 (1520° C.).

Titanium Compounds[1] occur more frequently in clays than is commonly supposed, though only in small quantities (under 2 per cent. titanium oxide), and in the ordinary methods of analysis it is (unconsciously) included in the figures for silica and alumina. Titanium compounds occur chiefly as *rutile* (TiO_2), *ilmenite* ($TiFeO_3$), *titanite* ($CaTiO_3$), *anatase* (TiO_2), and *brookite* (TiO_2), and act as somewhat powerful fluxes; hence, clays which are required to be highly refractory should not contain more than 2 per cent. Several investigators have independently examined the effects of titanium oxide on china clay and on artificial mixtures of alumina and silica. Their results (given in Tables XXI., XXIV., and XXV.) show that, within the limits in which this substance usually occurs in clays, the reduction in refractoriness is less than 40° C., and is therefore negligible if less than 2 per cent. of titanium oxide is present. Ten per cent. of this oxide lowers the softening point of kaolin about 100° C., but on fireclays richer in silica it has a considerably less effect (see figs. 16, 17, and 18).

Mixtures of calcium silicate and calcium titanite, according to Smolensky, form a solid solution at 1150°–1450° C., but do not become fluid below 1450° C. Titanium oxide in vitrified clays tends to produce a blue colour if less than 6 per cent. of titanic oxide is present, but this colour is easily discharged in the presence of iron compounds. At lower temperatures and if more than 6 per cent. of titanic oxide is present it tends to produce a yellow colour.

Tables XXI., XXIV., and XXV. show the results of experiments by R. Rieke[2]:—

TABLE XXI.—SILICA AND TITANIC ACID.

1.	Silica.		Seger Cone	36
2.	90 per cent. „	10 per cent. Titanic oxide.	„ „	33–34
3.	80 „ „ „	20 „ „ „ „	„ „	29–30
4.	70 „ „ „	30 „ „ „ „	„ „	26
5.	60 „ „ „	40 „ „ „ „	„ „	20[3]
6.	50 „ „ „	50 „ „ „ „	„ „	27
7.	40 „ „ „	60 „ „ „ „	„ „	30
8.	30 „ „ „	70 „ „ „ „	„ „	29
9.	20 „ „ „	80 „ „ „ „	„ „	29–30
10.	10 „ „ „	90 „ „ „ „	„ „	29
11.		Titanic oxide.	„ „	27

(*Information on titanium compounds continued on p.* 95.)

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[1] The use of titanium compounds as refractory materials was patented in 1878 by J. Giers, who specified the use of ilmenite or titanic iron ore, bonded with lime, and in 1909 by the British Thompson-Houston Co., who specified a mixture of titanium compounds with talc or clay and silicate of soda as bond.

[2] *Sprechsaal*, 1908, No. 30.

[3] Eutectic (see p. 33).

TABLE XXII.—EUTECTICS AND COMPOUNDS IN BURNED CLAY.

Substance.	Formula.	Percentage Composition.	Fusing-Point.		Observer.
			Seger Cone.	°C.	
Nepheline	$Na_2O.Al_2O_3.2SiO_2$	$21{\cdot}8Na_2O\ 35{\cdot}8Al_2O_3\ 42{\cdot}4SiO_2$	..	1223	A. S. Ginsberg.
Albite	$Na_2O.Al_2O_3.6SiO_2$	$11{\cdot}8Na_2O\ 19{\cdot}4Al_2O_3\ 68{\cdot}8SiO_2$	..	1200	Day and others.
Anorthite	$CaO.Al_2O_3.2SiO_2$	$20{\cdot}1CaO\ 36{\cdot}6Al_2O_3\ 43{\cdot}3SiO_2$	..	1550	U.L.Bowen
Eutectic between anorthite ($CaO\ .\ Al_2O\ .\ 2SiO_2$) and $Al_2O_3\ .\ 2SiO_2$	$CaO.2Al_2O_3.4SiO_2$ ..	$11{\cdot}2CaO\ 40{\cdot}7Al_2O_3\ 48{\cdot}1SiO_2$ $50{\cdot}1CaO\ 22{\cdot}9Al_2O_3\ 27{\cdot}0SiO_2$	15–16 19	1460 1560	R. Rieke. ,,
Eutectic between anorthite and $4CaO\ .\ Al_2O_3\ .\ 2SiO_2$	$2CaO.Al_2O_3.2SiO_2$	$33{\cdot}4CaO\ 30{\cdot}5Al_2O_3\ 36{\cdot}1SiO_2$	7	1275	,,
Eutectic between $4CaO\ .\ Al_2O_3\ .\ 2SiO_2$ and CaO	$6CaO.Al_2O_3.2SiO_2$	$60{\cdot}1CaO\ 18{\cdot}3Al_2O_3\ 21{\cdot}6SiO_2$	13	1400	,,
With a ratio Al_2O_3 and $3SiO_2$, the most fusible compounds lie between	$2{\cdot}5–5CaO.Al_2O_3.3SiO_2$	$33{\cdot}1–49{\cdot}7$ CaO $24{\cdot}1–18{\cdot}1$ Al_2O_3 $42{\cdot}8–32{\cdot}2$ SiO_2	6–7	1270	,,
Eutectic between wollastonite ($CaO\ .\ SiO_2$) and anorthite	$1(CaO.Al_2O_3.2SiO_2).$ $2{\cdot}33(CaO.SiO_2)$	$33{\cdot}9CaO\ 18{\cdot}5Al_2O_3\ 47{\cdot}6SiO_2$	..	1285	P. Lebedew.
Eutectic[1] between nepheline and anorthite	$1(CaO.Al_2O_3.2SiO_2).$ $2{\cdot}275(Na_2O.Al_2O_3.2SiO_2)$	$15{\cdot}6Na_2O\ 5{\cdot}8CaO\ 36{\cdot}0Al_2O_3\ 42{\cdot}6SiO_2$	..	1130	A. S. Ginsberg.
Another eutectic	55 per cent. anorthite and 45 per cent. nepheline.		..	1305	..
Eutectic between $Al_2O_3\ .\ 2SiO_2$ and $SrO\ .\ Al_2O_3\ .\ 2SiO_2$	$SrO.Al_2O_3.4SiO_2$	$18{\cdot}8SrO\ 37{\cdot}2Al_2O_3\ 44{\cdot}0SiO_2$	19	1565	R. Rieke.
$SrO\ .\ Al_2O_3\ .\ 2SiO_2$	..	$31{\cdot}7SrO\ 31{\cdot}3Al_2O_3\ 37{\cdot}0SiO_2$	30	1650	,,
Eutectic between $SrO\ .\ Al_2O_3\ .\ 2SiO_2$ and SrO	$2{\cdot}5SrO.Al_2O_3.2SiO_2$	$53{\cdot}7SrO\ 21{\cdot}2Al_2O_3\ 25{\cdot}1SiO_2$	8	1290	,,
Eutectic between $Al_2O_3\ .\ 2SiO_2$ and $BaO\ .\ Al_2O_3\ .\ 2SiO_2$	$BaO.2Al_2O_3.4SiO_2$	$25{\cdot}6BaO\ 34{\cdot}0Al_2O_3\ 40{\cdot}4SiO_2$	20	1590	,,
$BaO\ .\ Al_2O_3.\ 2SiO_2$	..	$40{\cdot}8BaO\ 27{\cdot}1Al_2O_3\ 32{\cdot}1SiO_2$	35	1710	,,
Eutectic between $BaO\ .\ Al_2O_3\ .\ 2SiO_2$ and BaO	$2{\cdot}5BaO.Al_2O_3.2SiO_2$	$63{\cdot}2BaO\ 16{\cdot}9Al_2O_3\ 19{\cdot}9SiO_2$	4	1220	,,
Eutectic between sodium metasilicate and calcium metasilicate	$1CaSiO_3.3{\cdot}8Na_2SiO_3$	$40{\cdot}6Na_2O\ 9{\cdot}6CaO\ 49{\cdot}8SiO_2$	..	932	H. S. van Klooster
Double silicate (?) of Na- and Ca-metasilicates	$2Na_2SiO_3.3CaSiO_3$	$20{\cdot}9Na_2O\ 28{\cdot}3CaO\ 50{\cdot}8SiO_2$	..	1175	,,
Eutectic between $2Na_2SiO_3\ .\ 3CaSiO_3$ and Ca-metasilicate	$1Na_2SiO_3.2{\cdot}45CaSiO_3$	$15{\cdot}2Na_2O\ 33{\cdot}6CaO\ 51{\cdot}2SiO_2$	..	1132	,,
Eutectic between CaO and α-Ca-orthosilicate	$2{\cdot}24CaO.1SiO_2$	$67{\cdot}5CaO\ 32{\cdot}5SiO_2$	..	2065	Day and others.
α-Calcium orthosilicate	$2CaO.SiO_2$	$65{\cdot}2CaO\ 34{\cdot}8SiO_2$	..	2130	,,
Conversion of α- into β-calcium orthosilicate	$2CaO.SiO_2$	$65{\cdot}2CaO\ 34{\cdot}8SiO_2$	..	1420	,,
Conversion of β- into γ-calcium orthosilicate	$2CaO.SiO_2$	$65{\cdot}2CaO\ 34{\cdot}8SiO_2$	..	675	,,
Eutectic between α-Ca-orthosilicate and α-Ca-metasilicate	$1{\cdot}26CaO.1SiO_2$	$54CaO\ 46SiO_2$	..	1440	,,
α-Calcium metasilicate (pseudo-wollastonite)	$CaO.SiO_2$	$48{\cdot}2CaO\ 51{\cdot}8SiO_2$	..	1540	,,
Conversion of wollastonite into pseudo-wollastonite	$CaO.SiO_2$	$48{\cdot}2CaO\ 51{\cdot}8SiO_2$	..	1190	,,
Eutectic between α-Ca-metasilicate and cristobalite	$CaO.1{\cdot}58SiO_2$	$37CaO\ 63SiO_2$	..	1426	,,
α-Magnesium metasilicate	$MgO.SiO_2$	$40MgO\ 60SiO_2$	..	1554	Kanolt.
Conversion of α-Mg-metasilicate into β-Mg-metasilicate	$MgO.SiO_2$	$40MgO\ 60SiO_2$	..	1375	Day and others.
Diopside	$CaO.SiO_2.MgO.SiO_2$	$25{\cdot}8CaO\ 18{\cdot}6MgO\ 55{\cdot}6SiO_2$	..	1391	,,
Eutectic between diopside and α-Ca-metasilicate	$1MgO.2{\cdot}29CaO.3{\cdot}46SiO_2$	$34CaO\ 10{\cdot}6MgO\ 55{\cdot}4SiO_2$	..	1357	,,
Diopside	$CaO.MgO.2SiO_2$	$25{\cdot}8CaO\ 18{\cdot}6MgO\ 55{\cdot}6SiO_2$	..	1363	P. Lebedew.
Eutectic between diopside and olivine	$2(MgO.FeO.SiO_2).$ $3(CaO.MgO.2SiO_2)$	$16{\cdot}8CaO\ 20{\cdot}3MgO\ 48{\cdot}5SiO_2\ 14{\cdot}4FeO$	..	1271	,,
Olivine	$MgO.FeO.SiO_2$	$23{\cdot}4MgO\ 34{\cdot}9SiO_2\ 41{\cdot}7FeO$	..	Above 1600	,,
Calcium orthosilicate	$2CaO.SiO_2$	$65{\cdot}1CaO\ 34{\cdot}9SiO_2$	16	1460	Hermann.
Eutectic between calcium orthosilicate and monticellite	$1MgO.1{\cdot}68CaO.1{\cdot}34SiO_2$	$43{\cdot}8CaO\ 18{\cdot}7MgO\ 37{\cdot}5SiO_2$	12	1375	,,
Monticellite	$CaO.MgO.SiO_2$	$35{\cdot}9CaO\ 25{\cdot}6MgO\ 38{\cdot}5SiO_2$	15	1435	,,
Eutectic between monticellite and $Ca_2SiO_4\ .\ 2Mg_2SiO_4$	$1CaO.1{\cdot}66MgO.1{\cdot}33SiO_2$	$27{\cdot}7CaO\ 32{\cdot}8MgO\ 39{\cdot}5SiO_2$	12	1375	,,
$Ca_2SiO_4\ .\ 2Mg_2SiO_4$	..	$24{\cdot}7CaO\ 35{\cdot}7MgO\ 39{\cdot}6SiO_2$	15	1435	,,
Eutectic between $Ca_2SiO_4\ .2Mg_2SiO_4$ and forsterite	$1CaO.4{\cdot}3MgO.2{\cdot}65SiO_2$	$14{\cdot}4CaO\ 44{\cdot}5MgO\ 41{\cdot}1SiO_2$	14	1410	,,
Forsterite (magnesium orthosilicate)	$2MgO.SiO_2$	$57{\cdot}1MgO\ 42{\cdot}9SiO_2$	16	1460	,,
Aluminium oxide (alumina)	Al_2O_3	..	..	2020	O. Ruff.
Sillimanite	$Al_2O_3.SiO_2$	$62{\cdot}9Al_2O_3\ 37{\cdot}1SiO_2$	..	1816	Day and others.
Eutectic between alumina and sillimanite	..	$63{\cdot}9Al_2O_3\ 36{\cdot}1SiO_2$	..	1810	,,
Eutectic between sillimanite and cristobalite	..	$7{\cdot}4Al_2O_3\ 92{\cdot}6SiO_2$	..	Under 1600	,,
Ferrous silicate	$FeO.SiO_2$	$54{\cdot}4FeO\ 45{\cdot}6SiO_2$	..	1100	W. Groume Grjimailo.
Ferrous calcium silicate	$4FeSiO_3+CaSiO_3$	$44{\cdot}6FeO\ 8{\cdot}7CaO\ 46{\cdot}7SiO_2$	..	1030	,,

[1] The nepheline-anorthite mixtures form an unbroken series of solid solutions.

TABLE XXIII.—EUTECTICS AND COMPOUNDS IN BURNED CLAY.

Substance.	Formula.	Percentage Composition.	Fusing-point, °C.	Observer.
Silica-Alumina Series.				
Mullite	$3Al_2O_3.2SiO_2$	..	1810	Bowers and Galig
Eutectic alumina-silica	..	Al_2O_3 5·5, SiO_2 94·5	1515	,,
Silica-Lime Series.				
Calcium metasilicate	$CaO.SiO_2$	..	1200	Rankin and Wright
Tricalcium disilicate	$3CaO.2SiO_2$	..	1475	,,
Calcium orthosilicate	$2CaO.SiO_2$	..	2130	,,
Tricalcium silicate	$3CaO.SiO_2$	..	1900	,,
Lime-Alumina Series.				
Tricalcium aluminate	$3CaO.Al_2O_3$	..	1535	,,
,, ,,	$5CaO.3Al_2O_3$	..	1455	,,
Calcium aluminate	$CaO.Al_2O_3$	..	1600	,,
,, ,,	$3CaO.5Al_2O_3$	..	1720	,,
Eutectic $3CaO.Al_2O_3$–$5CaO.3Al_2O_3$	..	CaO 50, Al_2O_3 50	1395	,,
Eutectic $5CaO.3Al_2O_3$–$CaO.Al_2O_3$	..	CaO 47, Al_2O_3 53	1400	,,
Eutectic $CaO.Al_2O_3$–$3CaO.5Al_2O_3$	..	CaO 33·5, Al_2O_3 66·5	1590	,,
Eutectic $3CaO.5Al_2O_3$–Al_2O_3	..	CaO 24, Al_2O_3 76	1700	,,
Magnesia-Silica Series.				
Forsterite	$2MgO.SiO_2$	..	1800	Bowen and Anderson
Clinoenstatite	$MgO.SiO_2$	..	1557	,,
Eutectic cristobalite-clinoenstatite	..	SiO_2 12·5, $MgO.SiO_2$ 87·5	1554	,,
,, periclase-forsterite	..	MgO 14, forsterite 86	1850	,,
Magnesia-Alumina Series.				
Spinel	$MgO.Al_2O_3$	..	2135	Rankin and Merwin
Eutectic spinel-magnesia	..	MgO 45, Al_2O_3 55	2030	,,
,, spinel-alumina	..	Al_2O_3 98, MgO 2	1925	,,
,, spinel-alumina [1]	..	Al_2O_3 92, MgO 8	1925	,,
Lime-Alumina-Silica Series.				
Anorthite	$CaO.Al_2O_3.2SiO_2$	..	1550	Rankin and Wright
Gehlenite	$2CaO.Al_2O_3.SiO_2$	..	1590	,,
Eutectic	..	CaO 23·25, Al_2O_3 14·75, SiO_2 62·00	1165	,,
,,	..	CaO 38, Al_2O_3 20, SiO_2 42	1265	,,
Magnesia-Alumina-Silica Series.				
Cordierite	$2MgO.2Al_2O_3.5SiO_2$	..	..	Rankin and Merwin
Eutectic	..	MgO 20·3, Al_2O_3 18·3, SiO_2 61·4	1345	,,
Lime-Magnesia Series.				
Eutectic	..	CaO 67, MgO 33	2300	,,
Silica-Lime-Magnesia Series.				
Eutectic	..	CaO 30·6, MgO 8·0, SiO_2 61·4	1320	Ferguson and Merwin
Magnesia-Lime-Alumina Series.				
Eutectic	..	CaO 51·0, Al_2O_3 42·7, MgO 6·3	1345	Rankin and Merwin
,,	..	CaO 41·5, Al_2O_3 51·8, MgO 6·7	1345	,,
Magnesia-Baryta-Silica Series.				
Eutectic	..	BaO 46, MgO 8, SiO_2 46	1120	..
Baryta-Silica Series.				
Barium disilicate	$2BaO.3SiO_2$	..	1450	Eskola
,, metasilicate	$BaO.SiO_2$	..	1604	,,
,, orthosilicate	$2BaO.SiO_2$	..	..	..
Eutectic	..	BaO 47, SiO_2 53	1374	Eskola
,,	..	BaO 60, SiO_2 40	1437	,,
,,	..	BaO 74·5, SiO_2 25·5	1551	,,
Lime-Ferric Oxide Series.				
Dicalcic ferrite	$2CaO.Fe_2O_3$	..	1436	Sosman and Merwin
Monocalcic ferrite	$CaO.Fe_2O_3$	..	1216	,,
Eutectic	..	CaO 8, Fe_2O_3 92	1203	,,
Soda-Silica Series.				
Sodium orthosilicate	$2Na_2O.SiO_2$	..	..	..
,, metasilicate	$Na_2O.SiO_2$	..	1089	Kracek
,, disilicate	$Na_2O.2SiO_2$	..	874	Bowen and Morey
Eutectic ortho-metasilicate	..	Na_2O 67, SiO_2 43	1022	Kracek
,, meta-disilicate	..	Na_2O 38, SiO_2 62	846	,,
,, quartz-disilicate	..	Na_2O 26, SiO_2 74	793	,,

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[1] Spinel forms a series of solid solutions with alumina.

TABLE XXIII.—EUTECTICS AND COMPOUNDS IN BURNED CLAY—*continued.*

Substance.	Formula.	Percentage Composition.	Fusing-point, °C.	Observer.
Ferrous Oxide-Silica Series.				
Ferrous oxide	..	..	1355–1377	..
Eutectic	..	FeO 78, SiO_2 22	1240	..
		FeO 60, SiO_2 40	995	..
Fayalite	$FeO.SiO_2$	..	1065	..
Ferrous orthosilicate	$2FeO.SiO_2$	..	1335	Herty and Fitteren
Silica-Potash Series.				
Eutectic $K_2O.SiO_2$–$K_2O.2SiO_2$	..	SiO_2 45, K_2O 55	780	Kracek, Bowen and Morey
Eutectic disilicate-tetrasilicate	..	SiO_2 69, K_2O 31	752	,,
Manganese-Silica Series.				
Eutectic	..	..	1175	Dverinckel and Greig
,,	..	..	1125	Smolensky
Potash-Soda-Silica Series.				
Eutectic [1]	..	Na_2O 15	745	Kracek
Felspar-Kaolin-Quartz Series.				
Ternary eutectic	..	felspar 92·5, kaolin 5, quartz 2·5	1300	Waldschmidt
Binary	..	felspar 95, quartz 5	1320	,,
Binary	..	felspar 92, kaolin 8	1300	,,
Titanium-Silica-Alumina Series.				
Eutectic	..	SiO_2 89·5, TiO_2 10·5	1510	Bunting
..	$TiO_2.Al_2O_3$	..	1860	,,
Eutectic	..	TiO_2 85, Al_2O_3 15	1715	,,
,,	..	TiO_2 38, Al_2O_3 62	1850	,,
,, $CaO.Al_2O_3.2SiO_2$–$CaO.TiO_2$	..	$CaO.TiO_2$ 35. $CaO.Al_2O_3.2SiO_2$ 65	1350	Nishioka
Ferrous Oxide-Alumina-Silica Series.				
Eutectic	..	FeO 62, Al_2O_3 3, SiO_2 35	980	Hay, White and Caulfield
,,	..	FeO 68, Al_2O_3 3, SiO_2 29	1002	,,
,,	..	FeO 72, Al_2O_3 3, SiO_2 25	1080	,,

[1] There are many eutectics with melting-points from 540° to 1470° C. (see Kracek, *J. Phys. Chem.*, 1932, **36**, 25, 38).

For further melting-points see the Phase-Rule diagrams by Hall and Insley, *J. Amer. Cer. Soc.*, 1933, **16**, 463–567.

Eutectics.—A eutectic is the mixture of two or more substances having the lowest melting-point of all the mixtures under consideration. Its composition is usually constant, but a eutectic is not usually a definite chemical compound.

Many eutectics occur in articles made from clay, though few of these are known to the manufacturers of such articles. In refractory materials the melting-point of any eutectic present is very important, as it determines the temperature at which the refractory material begins to lose its shape or even to collapse when heated under pressure.

Table XXII. shows the temperature at which the fusion of some important alumino-silicates, etc., occurs to such an extent that the sharp edges of the test pieces become rounded.

Table XXIII. contains the results of more recent investigations.[1]

A large number of other minerals occur in clays, but are of minor importance.[2]

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[1] In using these tables it should be noted that all the compounds will not be present, but only those for which the conditions of formation are favourable.

[2] See *British Clays, Shales, and Sands*, by A. B. Searle (C. Griffin & Co., Ltd., 1912), and the volume mentioned in the footnote on p. 33.

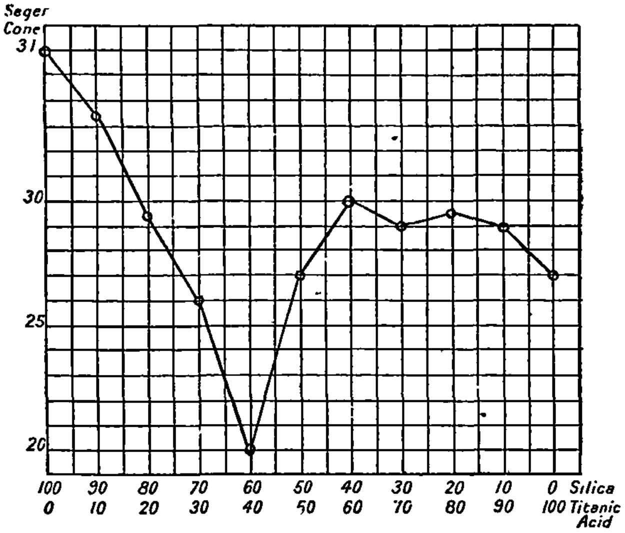

FIG. 16.—Effect of heat on mixtures of silica and titanic acid.

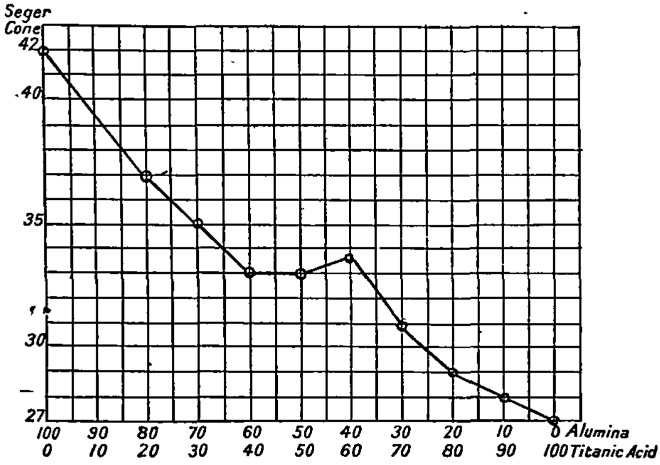

FIG. 17.—Effect of heat on mixtures of alumina and titanic acid.

TABLE XXIV.—ALUMINA AND TITANIC ACID.

1.		Alumina.			Seger Cone	42
2.	80 per cent.	,,	20 per cent.	Titanic oxide.	,, ,,	37
3.	70 ,, ,,	,,	30 ,, ,,	,, ,,	,, ,,	35
4.	60 ,, ,,	,,	40 ,, ,,	,, ,,	,, ,,	33
5.	50 ,, ,,	,,	50 ,, ,,	,, ,,	,, ,,	33
6.	40 ,, ,,	,,	60 ,, ,,	,, ,,	,, ,,	33–34
7.	30 ,, ,,	,,	70 ,, ,,	,, ,,	,, ,,	31
8.	20 ,, ,,	,,	80 ,, ,,	,, ,,	,, ,,	29
9.	10 ,, ,,	,,	90 ,, ,,	,, ,,	,, ,,	28
10.				Titanic oxide.	,, ,,	27

TABLE XXV.—KAOLIN AND TITANIC ACID.[1]

1.		Zettlitz kaolin.			Seger Cone	35
2.	90 per cent.	,, ,,	10 per cent.	Titanic oxide.	,, ,,	30
3.	80 ,, ,,	,, ,,	20 ,, ,,	,, ,,	,, ,,	26
4.	70 ,, ,,	,, ,,	30 ,, ,,	,, ,,	,, ,,	20
5.	60 ,, ,,	,, ,,	40 ,, ,,	,, ,,	,, ,,	20
6.	50 ,, ,,	,, ,,	50 ,, ,,	,, ,,	,, ,,	19–20
7.	40 ,, ,,	,, ,,	60 ,, ,,	,, ,,	,, ,,	20
8.	30 ,, ,,	,, ,,	70 ,, ,,	,, ,,	,, ,,	20
9.	20 ,, ,,	,, ,,	80 ,, ,,	,, ,,	,, ,,	26
10.	10 ,, ,,	,, ,,	90 ,, ,,	,, ,,	,, ,,	26
11.				Titanic oxide.	,, ,,	27

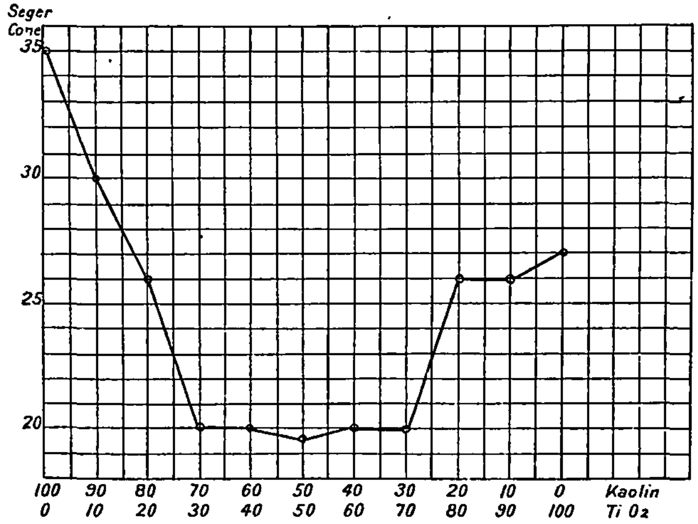

FIG. 18.—Effect of heat on mixtures of kaolin and titanic acid.

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[1] A similar investigation on Georgia kaolin and Laclede-Christy fireclay by Chalmer Bryce (*Trans. Amer. Cer. Soc.*, 1910, **12**, 533) gave similar but slightly lower results.

The most fusible mixtures of silicates and titanates of lime and baryta are (according to Smolensky)—

TABLE XXVI.

Base.	Formula.	Percentage Composition.	Fusing-Point.
Lime . .	$2CaSiO_3.1CaTiO_3$	45·5CaO 32·8SiO_2 21·7TiO_2	1420
Baryta . .	$1BaSiO_3.1{\cdot}09BaTiO_3$	68·4BaO 12·9SiO_2 18·7TiO_2	1376

Sulphur compounds occur in clays in the form of pyrite and marcasite (iron sulphides), and as gypsum and other sulphates. Sulphides are objectionable because of the odour produced when the clay is burned, the slag-like residue which disfigures the goods, and the difficulty often experienced in preventing the formation of a black " heart " or core.

Sulphates may dissolve in the water in the clay and rise to the surface of the goods, being carried thither by capillary attraction, and may form an objectionable scum.

Soluble sulphates, when added to a clay slip, make it stiffer and more plastic, aluminium and calcium sulphates being specially powerful in this respect. Sodium and potassium sulphates have only a feeble stiffening action. A solution of iron sulphate when added to a clay slip has the greater part of the iron absorbed by the clay, whilst the sulphate radicle remains in solution. Alumina is withdrawn in a similar manner from a solution of aluminium sulphate. No satisfactory explanation of this curious behaviour has yet been found, though it appears to be connected with the colloidal matter in the clay, as other colloidal sols behave similarly.

Gypsum does not usually occur to any great extent in fireclays, but its presence is very objectionable (see *Calcium sulphate*, p. 78).

In the presence of carbon monoxide and other reducing gases at 700° C., sulphates are reduced to sulphides.

Sulphates are dissociated, when heated, sulphur trioxide being volatilised at 800° C. to 1000° C., and the metallic oxide (soda, potash, lime, iron oxide, etc.) being left; they then do but little harm to the goods, except in so far as the metallic oxides reduce the fusibility of the material by forming fusible silicates. If an excess of free silica is present, the sulphates are decomposed somewhat more rapidly at about 900° C., the corresponding silicate being formed.

If a clay contains free alkali or a carbonate, and the fuel used in the kiln is pyritiferous, the latter will produce sulphur dioxide, which may combine with the alkali or carbonate and produce a sulphate or sulphite, with all the objectionable properties already described. This formation of sulphates in the kiln may be prevented by using coal free—or nearly free—from sulphur, and, in continuous kilns, by heating the goods to at least 120° C. with hot air instead of with fire gases.

Numerous other effects are attributed to " sulphur " by many kiln-men, but these have yet to be accurately proved. Orton and Stanley, who investigated the subject in 1908, consider that the loss of sulphur in the interior of the clay goods is usually very small, and that, in whatever form it may occur, sulphur is not likely to cause any serious disturbance until the clay becomes vitrified, after which the evolution of gas may occur, and a swollen and spongy body be produced. This is to a large extent prevented by heating very slowly with plenty of air so as to secure the complete combustion of the carbon at a temperature below 950° C., after which the volatilisation of the sulphur compounds follows easily and rapidly. As it is difficult to heat fireclays to a temperature high enough for the silica to react on the sulphates before all the carbon has been removed, the defects of swelling and slagging (which are so troublesome with some other clays) do not often occur with refractory clays, except as a result of carelessness on the part of the burner.

Cupriferous pyrites—chalcopyrite and bornite or erubescite—occur in some fireclays, notably those of Northumberland, Durham, South Scotland, North Staffordshire, and Shropshire. This term includes several compounds of sulphur, copper, and iron combined in various proportions. It is closely related to iron pyrite, and behaving in a similar manner, except that the stain produced in fired clay is green rather than black. Chalcopyrite is very similar to iron pyrite in external appearance though its colour is rather deeper. It has a specific gravity of 4·1 to 4·3 and a hardness of 3·5 to 4·0, and resembles iron pyrite in weathering very slowly.

Erubescite is readily distinguished from chalcopyrite and iron pyrite, as it has a reddish-brown colour and is much softer; its hardness is only about 3 on Mohs' scale. It has, however, a high specific gravity, 4·9 to 5·4, and, like marcasite, readily disintegrates on exposure.

When heated to redness, copper pyrites loses the greater part of its sulphur, and the resulting copper and iron oxides form a dark green slag. The proportion of copper pyrites present in a fireclay is seldom sufficient to be serious as regards the manufacture of firebricks, but special care should be taken to remove the nodules from clay used for the manufacture of large pieces of ware. It is a mistake to attempt to grind the copper pyrites to a fine powder; it is much better to allow it to remain in larger grains, which can then only spoil a relatively small number of articles, whereas if it is finely ground it will be more widely distributed, and almost all the articles may be spoiled. When copper sulphides cause trouble, it may be considerably lessened by stopping the grinding mill twice a day and throwing away the clay therein; such clay will contain the greater part of the sulphide.

Compounds of **phosphorus, vanadium, manganese,** and other elements are usually present in minute proportions in fireclays. Their invariable effect is to reduce the refractoriness of the clay, but the amounts present are usually too small for this effect to be appreciable without special tests.

Vanadium compounds cause a greenish discoloration in some buff-burning clays of the Coal Measures when exposed to moist air; but as this discoloration can be washed off with water—like the "scum" from soluble salts—it is not a serious disadvantage. By heating the clay until it is partly vitrified, Seger found the colouring agent was rendered insoluble and the discoloration prevented.

Manganese oxides are of three kinds—the monoxide MnO, the dioxide MnO_2, and the tetroxide Mn_3O_4.

Rieke[1] has found that when manganese monoxide is added to a china clay or kaolin, or to a mixture of alumina and silica in the same proportions, it reduces the refractoriness of the clay as follows:—

[TABLE XXVII.

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[1] *Sprechsaal*, 1910, No. 16.

TABLE XXVII.—EFFECT OF MANGANESE MONOXIDE ON KAOLIN.

Molecules.		Per cent. MnO.	Fusing-Point in Seger Cones.
$Al_2O_3+2SiO_2+$	MnO	..	..
	0·25	7·38	30
	0·5	13·73	12
	1	24·15	About 1
	1·5	32·32	„ 01
	2	38·90	„ 03–02
	2·5	44·32	„ 02
	3	48·85	„ 01

The following table shows the melting-points of various manganese compounds[1]:—

TABLE XXVIII.—MELTING-POINTS OF MANGANESE COMPOUNDS.

Silicate.	Formula.	Percentage Composition.	Melting-Point.	Observer.
Manganese metasilicate (rhodonite) . .	$MnO.SiO_2$	54·1MnO 45·9SiO_2	°C. 1210 1210 1230	P. Lebedew. W. Groume Grjimailo. Doerinkel.
Manganese orthosilicate (tephroite) . .	$2MnO.SiO_2$	70·2MnO 29·8SiO_2	1323	Doerinkel.
..	$7MnSiO_3+CaSiO_3$	47·9MnO 5·4CaO 46·7SiO_2	1184	W. Groume Grjimailo.
Eutectic between SiO_2 and MnS .	$MnS.13{\cdot}3MnSiO_3$	51·5MnO 43·8SiO_2 4·7MnS	1130	A. Woloskow.
Manganese sulphide MnS .	..	..	Over 1150	A. Woloskow.
Eutectic between $MnSiO_3$ and $MnTiO_3$ . .	$MnTiO_3$ 3·48$MnSiO_3$	52·3MnO 34·6SiO_2 13·1TiO_2	1120	Smolensky.
Manganese titanate . .	$MnTiO_3$	47·0MnO 53·0TiO_2	1404	„

Uranium oxide,[2] when added to Zettlitz kaolin, decreases the fusion point, until 50 per cent. of the oxide has been added; larger proportions increase the fusion point. The eutectic fuses at Seger Cone 15.

The action of various other fluxes upon finely washed kaolin is shown in the following table[3]:—

TABLE XXIX.—EFFECT OF FLUXES ON KAOLIN.

Material.	Melting-Point. °C.
Kaolin alone	1780
„ +15 per cent. chromium oxide .	1810
„ +20 „ glass . . .	1710
„ +50 „ „ . . .	1710
„ +20 „ lithium carbonate .	1330
„ +50 „ slag . . .	1700
„ +20 „ zinc oxide . .	1760

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[1] *Sprechsaal Kalr.*, 1914.

[2] O. Kallauner & J. Hruda, *Sprechsaal*, **55**, 523 (1922).

[3] *Rev. de Metall.*, 1904, ii. 92.

Organic matter is a frequent constituent of clays; particularly of those which are plastic, and some chemists consider that the plasticity of clays is due in some way to this material. The organic matter may be of animal or vegetable origin, but in either case it is distinguished by the fact of its being composed of carbon, hydrogen, and oxygen, and is driven off by heating the clay slowly in the presence of sufficient air. Organic matter contained in clays may be derived from (1) infiltration of soil suspended in water into a bed of clay; (2) the deposition of the clay on land containing vegetable matter, the existence of animals and plants on the surface of the deposit, or the presence of animals and plants carried by the water at the same time as the clay; (3) various bituminous rocks which become mixed with the clay. In the first and third cases the proportion of organic matter is not usually large, but in the second it may become so. As its origin is usually of minor importance and its carbon content is an essential characteristic, the term *carbonaceous matter* is frequently used. This has the further advantage of including such organic material as has undergone so complete a change as to render it almost impossible to describe it in more definite terms. Indeed, the composition of the major part of the organic matter in clays is very imperfectly understood. This organic matter has apparently played an important part in the formation of fireclays, especially in the production of iron sulphide (*pyrite*).

Carbonaceous matter may be present in such a form that its vegetable or animal nature is clearly recognisable, in the form of leaves, wood, roots, etc., and as such is frequently found in surface clays. The fossilised remains of animals and plants are found in most fireclays, but these are usually little more than facsimiles of the original, the carbonaceous matter having been largely replaced by earthy material.

In the form of humus, peat, lignite, coal, shale oil, and bitumen, or materials allied to these, carbonaceous matter occurs frequently in fireclays. If not excessive in amount, and if present in a finely divided state, such material is often an advantage, as it reduces the amount of fuel needed to burn the clay in the kilns. If irregularly distributed, and in large fragments, however, it may cause uneven burning, and may be a source of perpetual annoyance and trouble. The precautions necessary for the successful working of clays rich in carbonaceous matter are given later.

Clays or shales containing more than 10 per cent. of carbon can seldom be worked profitably; even half this amount sometimes produces black cores or "hearts," and necessitates such slow burning as to waste fuel. W. Ayrton, in 1880, patented a process for removing organic matter from clays; it consisted of exposing the ground clay to a stream of slightly alkaline water, the flow being regulated so that "nearly pure silicate of alumina is carried away and settles in the first vat." The obvious effect of the absorbed alkali in reducing the refractoriness of the clay appears to have been overlooked.

The colour of clay is seldom any guide as to the proportion of carbonaceous matter present, though the darker clays are often rich in this substance. That the colour of many raw clays is due to it may be concluded from the fact that they change their colour on being heated, though this is by no means a reliable criterion.

The effects of carbonaceous matter in clay are numerous. The most important are on: (1) the colour before and after drying; (2) the plasticity of the clay; (3) the size and number of the pores in the fired clay (porosity); (4) the quantity of water the clay can absorb, and consequently its shrinkage; (5) the smaller amount of fuel required to burn the clay, except when the carbonaceous matter creates special difficulties in firing.

The action of organic matter in rendering a clay more plastic is rather obscure, and liable to be confused with a " stickiness " or adhesiveness which is not true plasticity. Thus, the true plasticity of a clay is not increased by mixing it with a solution of glue, flour, or starch, though such treatment will sometimes confer a pseudo-plasticity on some lean clays and non-plastic powders. At the same time, there is little reason to doubt that some clays do owe part of their adhesiveness to a viscous form of organic matter (humus).

The artificial creation of this pseudo-plasticity is not usually desirable, as defective clays to which such organic materials have been added do not usually possess the required characteristics. Where a mixture is not sufficiently plastic, the better method is either to substitute a more plastic clay for a " lean " or " short " one, or for part of the non-plastic material, the selection of the clay so added depending on what is required. In most cases, the addition of a ball clay is quite satisfactory, but cheaper clays may sometimes be used if the composition of the mixture permits of sufficient adjustment.

The most troublesome effect of carbonaceous matter is that due to the fact that carbon has a more powerful affinity for oxygen than has iron, and so it will keep any iron oxide in a clay in a reduced (ferrous) state ; and as this is objectionable on account of the great fusibility of ferrous silicates, it is necessary to exercise great care to burn off the carbon with a plentiful supply of air, without allowing the temperature of the clay to rise sufficiently for the reduced iron oxide to form a black fusible slag or core. The amount of trouble and attention involved in this will depend on whether the pores in the clay are large or small. It is exceedingly difficult to avoid the formation of this slag at the high temperatures at which the fireclays are burned.

Water occurs in three forms in clays: (*a*) as moisture or dampness; (*b*) as water of formation, this being that which is added to produce a workable paste; and (*c*) combined water.

The moisture in a clay is sometimes troublesome, as it may produce a sticky adhesive material which is difficult to manipulate and must therefore be dried or mixed with some absorbent, such as burned clay (grog), very dry clay, or sand. Usually when the clay has been made into bricks or other articles of definite shape, the moisture becomes part of the " water of formation," but it is in the grinding of the clay that the presence of moisture *per se* is apt to be troublesome.

Clay is naturally hygroscopic, and when fully dried and then exposed to the air it rapidly absorbs moisture from the latter, even though it may not become actually wet.

Water is added to clay for a definite purpose, viz., to make it of convenient consistency and plasticity, and cannot, unless it be present in excess, be regarded as an impurity. Any excess of water may usually be removed by exposing the clay to the atmosphere, or, more rapidly, to a current of warm air. If the clay has been made into articles of definite shape, however, great care is necessary to prevent cracking.

Most analyses of clay show the proportion of moisture correctly, but the combined water is included under " Loss on Ignition," with carbonaceous matter, sulphur, carbon dioxide (from any carbonates present), and sulphur trioxide (from any sulphates), and therefore its amount is seldom known. Strictly speaking, this combined water does not exist as water in the clay, but when the clay is heated it decomposes, and one of the products is water.

The effect of water on clays containing it largely depends on the form in which it is present.[1] If it exists as moisture or water of formation it makes the material plastic and generally workable, and as it evaporates (by drying) the material shrinks in size (see *Shrinkage*), and may crack if the water is removed too rapidly. If too little water is present, the material will be too stiff to be readily shaped, though usually it may be more easily crushed than when in a moist condition. If a large quantity of water is mixed with clay a slip or slurry is formed, from which many of the coarser impurities may be separated by allowing the slurry to remain stationary for a short time and then running off the fluid portion. Instead of allowing the slip or slurry to stand, it may be passed through fine sieves or through a suitable centrifugal separator, and so freed from coarse particles. If a slip or slurry is allowed to stand sufficiently long, the solid matter will settle and the greater part of the water may then be poured off and so separated.

The combined water is quite different. It is only expelled at a temperature of 400° C. to 600° C.,[2] and is accompanied by a slight shrinkage; the clay then loses its plasticity and cannot recover it by any treatment yet devised, but becomes hard and stony. It is, indeed, probable that this so-called water is only formed when the clay molecule begins to decompose in consequence of its being heated.[3]

The **physical and chemical properties** of a fireclay[3] must be such as to give it great refractoriness, combined with some ability to withstand sudden changes in temperature, and a texture which will enable it to endure satisfactorily if the clay is to be used for the manufacture of bricks or blocks which will be exposed to the action of molten slags or acids at high temperatures. The effect of various impurities on fireclays has been shown on pp. 67-101, and from what is therein stated, it will be realised that far more complex reactions occur than is usually supposed, and that the popular idea that the refractoriness of a clay is reduced in direct proportion to the amount of base added or of impurity present is not always correct. The foregoing tables also explain why the addition of a large amount of "flux" may increase the refractoriness of a mixture, whilst the addition of a refractory substance (*e.g.* silica) may make a clay more fusible.

The *colour* of fireclays, as mined, is usually grey or somewhat bluish, though some refractory shales are brown. The colour of the Coal Measure fireclays is due to minute particles of organic matter, disseminated throughout the clay by the action of the water, and to a less extent to mineral matter. Imprints of vegetation—the knotted stems and branches of trees—or shells are also frequently found in a very perfect condition. In some places the colour of the clay closely resembles that of freshly cut Millstone Grit, and the fireclay is then usually coarse in texture, rich in free silica and also in iron oxide.

In other places, fireclays are black, with bright cleavage surfaces; but are then inferior in quality, vitrifying at a lower heat, and too full of deleterious substances to be useful, though they are then usually plastic and of an oily nature.

In fireclays found near the surface, the colour is sometimes almost white, with slight markings and traces of iron oxide, or a mottled grey and yellow colour, with much strong, red ochre-like matter in it.

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[1] Information on the effect of added water will be found on p. 104.

[2] Some clays appear to decompose at a much lower temperature, but the rate of decomposition is then extremely slow.

[3] For much fuller information see the author's *Chemistry and Physics of Clays and Other Ceramic Materials* (Ernest Benn, Ltd.).

The *texture* of a fireclay should be homogeneous, without laminations, except such as may be caused by the thin markings due to the fine veins of coal, and it should be free from any obvious grains. A few of the secondary qualities and of the very siliceous fireclays are found in well-marked layers, and are both laminated and striated. The texture of a good fireclay should be fine, apparently slightly greasy on a freshly cut surface, and free from excessive grittiness.

Fireclays are usually sufficiently indurated to make it difficult to determine the *size of their particles*. Most of the particles are so small that when gently rubbed with water they will pass completely through a sieve with 200 holes per linear inch, and a considerable proportion will be carried away by a stream of water flowing at the rate of 0·18 mm. per second or 0·036 foot per min. Most fireclay particles are, however, coarser than those of ball or china clay,[1] though this may be more apparent than real; their essential ingredient appears to be amorphous.

The *specific gravity*, or density, of fireclays varies between 2·6 and 2·75, according to the extent to which they are indurated.

The *hardness* of fireclays varies considerably; all can be cut with a knife, though some portions are hard enough to scratch glass; these latter are usually rich in impurities of a quartzose nature.

Fissility—or the capability of being split up into slabs or thin flat pieces, or even into flakes or foliations—is characteristic of many indurated clays, and especially of shales. If the splitting can be effected so as to form plates of extreme thinness, the material is said to be laminated; if the tendency to split is strongest in the direction of bedding, the material is termed shaly; if this tendency is strongly marked in any other direction, it is said to be fissile, as are slates and certain limestones and sandstones.

The *magnetic properties* of fireclay have not been extensively studied. The feeble magnetism shown by some burned fireclays is due to the conversion of part of the iron oxide into magnetite (magnetic iron oxide), or of other minerals capable of affecting a magnet. Sidot has shown that at a " white heat " ferric oxide is converted into magnetite and so becomes magnetic. So far as is known, clay is in itself non-magnetic; but in addition to the well-known magnetic minerals (of which magnetite is typical), several feebly magnetic ones occur in clays, the most important being limonite, hæmatite, pyrite, and chalcopyrite, though unless they were formed during the cooling of the kiln it is difficult to see how such materials could retain their magnetism when made into bricks. Hopwood has drawn attention to the fact that some black specks (probably magnetite) present in many clay wares are magnetic, as are all ferrous silicates. Zirkel has found that fused phyllite ($FeO.Al_2O_3.SiO_2$) is magnetic.

The *conductivity* of clays for electricity is tolerably constant for the raw material, but varies considerably in the fired goods, and it is only when the latter are used for electrical instruments, etc., that it becomes important commercially.

The electrical conductivity of clays may prove of value in its purification in two ways: (*a*) in purifying clay slips by kataphoresis (Schwerin's " Electro-osmose " process), and (*b*) on finely powdered clays by electrostatic means, as Blake, Morscher, and Swarte have patented machines for separating good conductors from other materials; the most important to the clayworker are—

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[1] Some fireclays require boiling with water containing a little alkali to decompose any organic acids they contain, and to deflocculate the particles before they can be completely separated by water.

Good Conductors.—Native minerals, magnetite, magnetic hæmatite, chalcopyrite, erubescite, pyrrhotite, graphite, magnetic ilmenite, molybdenite, copper glance, argentite, metallic sulphides, tellurides, chromite, wolframite.

Moderately Good Conductors.—Biotite, tourmaline, titanite, rutile, anatase, brookite, cassiterite.

Bad Conductors.—Zircon, corundum, fluorite, barite, and most minerals free from iron, quartz, sandstone, granite, porphyry, schist, spinel, calamine, gypsum, and silicates, including clays.

Blake, Morscher, and Swarte's process has not, however, been applied successfully to clays on account of the small size of the particles. Schwerin's electro-osmose process for the purification of clays has attracted much attention.

The electrical conductivity of clays is also important in studying their physico-chemical nature, particularly their viscosity and plasticity.

The *absorption* of water by fireclay may conveniently be studied from three points of view—

(*a*) When the amount of water absorbed is relatively slight. This is termed *hygroscopic water.*

(*b*) When water is added to convert the clay into a plastic mass. This is termed the *water of formation.*

(*c*) When water is added in a sufficient quantity to convert the clay into a cream or slurry.

When any clay is completely dried, either naturally or without having been excessively heated, it is highly *hygroscopic* and absorbs moisture readily—sometimes up to 20 per cent. of its weight—without becoming appreciably moist. It is, therefore, extremely difficult to keep clay perfectly dry, and most specimens contain a considerable percentage of moisture.

Seger considered that the hygroscopic nature of clay enables it to be distinguished from silt and fine sand, as these do not so readily absorb moisture from the air.

When a piece of air-dried clay is placed in water the latter enters the pores and drives out the air, lifting up the smallest particles of clay. This disturbs the structure of the material, and a partial or complete breakdown occurs. The absorption of water is accompanied by a slight rise of temperature; this, though scarcely noticeable, is characteristic.

The amount of water absorbed varies greatly with different clays; in some cases it is equal to 80 per cent. of the weight of the clay.

Rohland suggests that this power of imbibing a definite amount of water is due to the colloids in the clay, and that as soon as a clay has absorbed sufficient water to disperse its colloids and to form a colloidal solution its ability to absorb water reaches a saturation-point and ceases; this is proportional to the colloids present, and probably, roughly, to the plasticity of the clay. It may, however, be proportional to certain capillary spaces between the clay particles, though not to the porosity of the clay, as the large pores may be unable to retain so much water by capillary attraction in proportion to their size.

If the amount of water is sufficiently large, and particularly if it is slightly alkaline, the clay will gradually soften (or slake) and fall into a slimy powder, the time required varying with different clays from a few minutes to several months. Sokoloff considers this due directly to the same causes as the plasticity of the clay.

In the manufacture of articles, it will be found that each kind of clay requires a definite proportion of water for its efficient manipulation. If more is added the clay becomes weak; if less it will be too short. The amount of water needed for the purpose is less in proportion as the ratio of non-plastic material in the body increases. Therefore, the leaner the clay, the less water it will need to temper it. This water is known as *water of formation*, and its amount has a theoretical as well as a practical importance, being closely related to plasticity. Unfortunately, there is no certain method of measuring the consistency of clay paste nor of ascertaining when the correct proportion of water has been added to a clay. The ordinary method consists in adding a definite quantity and working it up in a paste. If this paste adheres to the fingers, too much water is present; if it cannot be worked into a smooth paste which readily receives the impressions of the finger-prints, but does not adhere to the skin, more water must be added. After a few trials the correct amount of water may be ascertained, but the test is too rough for scientific purposes.

The most suitable amount of water to be added to clays to form good modelling paste varies enormously. In some cases, only 5 per cent. is needed, in others it may be equal to more than half the weight of the clay used. If to a moderately plastic dry clay, water is added in increasing quantities, the clay can at first be moulded with difficulty, then more easily, and finally, it may be formed with the greatest facility. But if, after this amount, the proportion of water is still increased, the clay begins to adhere to the fingers, and it soon becomes impossible to form it into a definite shape.

If the formation is done by mechanical means, by which the clay is subjected to a greater pressure, less water must be added to the body, in order to obtain the same plasticity, and it will be expedient to make it of a stiffer consistency. Pressure in this case plays the same part as water in relation to the plastic qualities of clays; the one can be partially replaced by the other, so that if the pressure is increased the proportion of water should be diminished, and *vice versâ*.

Bourry has observed that: (1) With a clay of definite plasticity there exists a maximum of pressure and a minimum of consistency, between which the clay can be given a definite form. If the clay is too plastic, this maximum pressure will be less, and, on the other hand, the minimum of consistency will be too great to permit formation by hand or by a slight pressure. If the clay is too short, the maximum pressure will become considerable, and the minimum consistency will yield a body which is too liquid to be shaped.

(2) With a mode of formation corresponding to a pressure and consistency which are fixed, the plasticity of the clay employed can only vary between certain limits. If it is too plastic it will adhere to the moulds; if too short its grains will not unite among themselves, and it will be impossible to make a compact mass of them. It is, therefore, of the highest importance that a careful choice should be made of the mode of formation for a body of a given plasticity, or to produce in a given body the plasticity suitable for a given mode of formation.

If a sufficient quantity of water is added to a clay, and the whole thoroughly mixed, a slip or slurry will be produced which has certain characteristics, according to the proportion of water and clay, to the nature of the clay and the purity of the water. If the proportion of water is very large and the clay particles difficult to separate, they may fall to the bottom of the water soon after the mixing ceases, or the greater part of them may so fall, leaving the smallest particles suspended in the water for many hours.

Slips containing about an equal weight of clay and water are largely used in various branches of clayworking, for covering other clays of inferior colour when burned and for making objects by the process of *casting*. In the former, the articles to be covered are immersed in the slip, and in the latter the slip is poured into plaster moulds and allowed to remain for a short time, after which any superfluous slip is poured away. On allowing the mould to dry, the water is absorbed by the plaster, and the clay article may be removed in due course.

In both cases it is necessary that the proportions of clay and water should be carefully adjusted in order to obtain the best results. When a suitable mixture has been obtained it will usually be sufficient to weigh exactly one pint of it accurately, and to dilute other mixings with stronger slip or with water until they reach the same weight per pint. The specific gravity of the slip may be determined with greater exactness in a pycnometer, if desired, but for most purposes this involves unnecessary trouble.

Schwerin has found that water and alkalies in a clay slip may be removed by electro-osmosis, by connecting the bottom of the tank containing the slip with the negative pole and a hollow roller with the other pole of a battery, when the water and alkali will collect at the bottom, and the clay, in the form of a soft paste, on the roller.

The *viscosity* of clay slips is a characteristic property, and throws some light on the peculiar physical nature of clays. The viscosity of a fluid may be regarded as its resistance to flowing, and is usually measured by ascertaining the time taken by a given volume of the fluid to flow through a given orifice when under a constant pressure. In order to eliminate difficulties due to a portion of the material being deposited, and so making the flow irregular, some means of keeping it in motion may be necessary. Mellor, Green, and Baugh used a modification of the Marriott flask (fig. 19), which prevents the slip from settling by the air bubbles drawn through it. Viscosity may also be measured, as suggested by Bleininger and Brown, by immersing a light shaft carrying paddles in a given volume of the slip, and noting the time taken by a given force to produce a definite number of revolutions of the paddles.

By treating distilled water in the same manner as the slip, and dividing the figures obtained for the latter by those for the former, a ratio is obtained which is of considerable value in comparing the viscosities of different clays, or of the same clay to which various substances have been added.

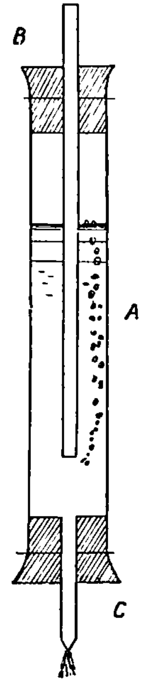

FIG. 19.—Marriott flask.

Mellor, Green, and Baugh found the following changes in the viscosity of a standard body slip, consisting of 16 grammes ball clay, 19 grammes china clay, 13 grammes Cornish stone, 20 grammes flint, and 100 cubic centimetres of water, when 0·1 to 6 grammes of various substances were added :—

1. The slip is first made thinner and then thickened by the addition of sodium carbonate, potassium carbonate, fusion mixture, potassium hydrogen sulphate, potassium bisulphate, caustic potash, potassium nitrate, sodium sulphide, tannin, and gallic acid, the effect varying according to the amount added.

2. The slip is first thickened and then made thinner by the addition of copper sulphate, dilute ammonia, and potassium aluminium sulphate.

3. The slip is made thinner by the addition of magnesium sulphate, mercury sulphate, sodium sulphate, sodium sulphite, sodium acetate, sodium chloride, sodium phosphate, ammonium gallate, hydrochloric acid, and water-glass.

4. The slip is thickened by the addition of grape sugar, humic acid,

ammonium chloride, calcium chloride, calcium sulphate, aniline, ethylamine, methylamine.

5. The viscosity of the slip is not affected by alcohol.

Some of the substances in groups 3 and 4 may have to be transferred to groups 1 and 2 if greater or smaller concentrations are employed.

Weber has stated that most soluble sulphates increase the viscosity of a clay slip, but their effect may be neutralised by the addition of a solution of barium hydroxide. The most harmful sulphates, according to this investigator, are those of calcium, aluminium, and the heavy metals. Alkali sulphates stiffen the slip when only 0·1 per cent. is present; larger proportions render it thinner, until more than 1 per cent. is present, after which they stiffen it again. Zinc and copper sulphates exhibit this phenomenon of variable influence in a marked degree.

Bleininger found that the first addition of clay (up to 3 per cent.) to water decreased the viscosity of water on account of the deflocculation of the clay by dilution and the solution of the contained electrolytes. When, however, the addition of clay became so great that no further matter went into solution, and the effect of the gel showed itself, the viscosity increased with each addition of clay. This negative viscosity is peculiarly characteristic of some clays. Simonis, Bleininger, and others have suggested that there is a direct connection between the viscosity of a clay slip and the plasticity of the clay from which it is made, the plasticity being considered to be represented by the amount of water which must be added to produce a slip of definite viscosity. This definition of plasticity is by no means complete, as the viscosity of a clay slip is really a measure of the amount of coagulated colloid material in it, and, therefore, indirectly of the plasticity due to this cause. As the various properties of clay summarised under the term " plasticity " are, in all probability, not due exclusively to the presence of colloid matter, it appears unlikely that plasticity can be completely measured in terms of viscosity, though this latter property may prove sufficient for many purposes.[1]

The *viscosity of clay paste* is an important factor in the manufacture of bricks, etc., by " expression." A paste which is too fluid cannot be used for this purpose; one which is too viscous will require too much power to force it through the die of the machine. It has also been used by Bingham and others as a means of measuring plasticity. According to these investigators the chief difference between a fluid and a plastic paste is that immediately pressure is applied to a fluid it begins to flow, whereas with a plastic paste a certain critical pressure (known as the " yield-value ") must be reached, after which the paste flows like a fluid.[2]

The addition of very small quantities of *acids* or *alkalies* to a clay paste may make a very large difference in its fluidity or viscosity. Thus, if an alkali is added to a viscous clay slip or clay paste the latter will become more fluid until a certain limit is reached, after which it will become stiff again.

According to Rohland, the addition of hydrochloric, nitric, sulphuric, acetic, or propionic acid increases the plasticity of a clay slip by coagulating the colloid matter present. Solutions with an acid reaction such as sal ammoniac, aluminium chloride, ferric chloride, and bichromate of potash behave similarly. Alkalies, such as ammonia, caustic soda, caustic potash, lime-water and baryta, and basic salts, make the slips more fluid and reduce the plasticity of the material, but their behaviour depends on their concentration. The liquefying action of

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[1] For further information on the viscosity of clays see the author's *Chemistry and Physics of Clays and Other Ceramic Materials* (Ernest Benn, Ltd.).

[2] Many fluids have a small yield-value, but it is usually of negligible dimensions.

various alkaline salts on clay is due to their hydrolysis, and to the action of the resultant negatively charged OH-ions, which repel the similarly charged clay particles and increase the dispersion, thus breaking the larger particles into smaller ones. If there is an excess of soluble salts present, the concentration of the OH-ions increases, and a "stiffening" of the mass will occur. Organic colloids act similarly to alkaline salts, but also protect the particles and make the liquid less sensitive to the action of flocculating agents; an organic colloid present in a clay may, therefore, render the maximum liquefaction of the clay impossible. The very small proportion of alkali needed is remarkable. For instance, a clay slip containing 50 per cent. of its weight of water will retain in suspension nearly twice as much clay if 0·001 per cent. of soda is added, or alternatively only half the proportion of water need be present. The control of the fluidity or viscosity of clay slips by the addition of very small quantities of acid or alkali is used commercially in regulating the proportion of solid matter in suspension, the rate of settlement of suspensions, and the plasticity of clay pastes. These properties are used in the preparation of slips for casting thick ware, in purifying clays and in other ways. There are considerable differences of opinion as to what are the precise forms in which the acid or alkali radicals are attached to the clay.

The fluidity of clay slips is of great importance in casting, particularly when small quantities of alkali are added, as in Weber's process (see Chapter XII.).

The *plasticity* of fireclays is not so marked as that of the ball clays, but it is sufficiently great to enable blocks of all shapes to be produced. The moderate plasticity of fireclays is a great advantage, as highly plastic clays present many difficulties to the user.

Plasticity may be defined as that property of a material which enables it to change its form without rupture, the new shape being retained when the deformative force is removed. In other words, a material is said to be plastic when it can be kneaded or pressed into a desired shape, and remains in that shape when the kneading ceases or the pressure is removed; this alteration of shape being capable of being repeated indefinitely. Thus, a brickmaker terms a clay plastic when it will work well in his machine or is capable of being kneaded into a "good" paste; but a potter usually places more emphasis on the binding power of a clay, though he terms this its plasticity.

Although these definitions are sufficient for practical purposes, they are not entirely satisfactory, nor is there any explanation of the causes of plasticity which meet all the needs of the case.

Several investigators have confused plasticity with other properties such as tensile strength; Gront, Zschokke, Pfefferkorn, Jochum and Hyslop appear to do this.[1] It is important to distinguish between the actual, the latent, and the potential plasticity.

Actual plasticity is the plasticity of the material at the moment of its consideration.

Potential plasticity is the plasticity which can be developed in the material by suitable treatment, such as (*a*) the addition of water, (*b*) more thorough mixing so as to distribute the water present more uniformly, (*c*) the removal of non-plastic material or other impurity, (*d*) the addition of acid or alkali, (*e*) prolonged storage (*e.g.* "souring" or "weathering").

Latent plasticity is the difference between potential and actual plasticity; it is that increase in plasticity which can be produced by suitable treatment.

When most fireclays are freshly obtained, the actual plasticity is small;

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[1] Clews, Macy and Rigby, *Chem. Ind.*, 1938, **57**, 223.

it must, therefore, be increased by one or more of the treatments just mentioned.

As already stated, most clays require the addition of a suitable amount of water before they become appreciably plastic, but other liquids may be used if convenient, though they sometimes produce quite different characteristics. Thus, glycerine may be used, but prevents the clay from drying; and Krupsay has pointed out that if plastic masses made from clay with water and oil respectively be kneaded together the resulting mixture is quite non-plastic. Fatty liquids, such as oils, which are used by some crucible makers, seem to make a more plastic body than water, especially if the clay has been previously dried to dispel the hygroscopic water, but some mineral oils, including engine oil, benzoline, and petrol, do not develop plasticity, as they have not this power of forming a film round the grains, with the result that the mass behaves like sand and water, there being insufficient cohesive action to hold the particles together.

Plasticity does not appear to depend on the composition of the clay so far as the proportions of the various constituent materials are concerned, though for some unexplained reason, clays (alumino-silicic acids) possess this property more strongly than other minerals, and when a plastic clay is heated to a temperature at which it is decomposed, the plasticity is lost and cannot be restored again by any commercial method if the dissociation is complete; several investigators claim to be able to restore the plasticity of only slightly burned material. It is interesting to note that if clay is decomposed into free silica and free alumina when heated, the resultant particles should be smaller than those of the original clay, and if plasticity were chiefly due to the smallness of the particles, it should not be difficult to make lightly, yet completely, calcined clay plastic. Nevertheless, the shape or size of the particles does seem to be connected with plasticity, and Le Chatelier claims that the lamellar structure of the clay particles and their strong capillary attraction are the cause of the plastic character of the mass. He concludes that the tension between the air and water surfaces in the capillaries between the particles prevents rupture under pressure, yet allows the particles to roll over each other so that the mass can be moulded into any desired shape with ease, the clay remaining in the new shape without in any way attempting to regain its original one. In support of this conclusion, he states that all moist, fine powders possess some plasticity and, after kneading with the fingers, acquire some degree of hardness on drying. He found that mica or glauconite, after prolonged grinding, produced a material something like clay and equally as plastic.

H. G. Schurecht[1] suggests the following relationships between the size and compactness of the clay grains and the plasticity of a clay:—

1. Loosely cemented aggregates of kaolinite grains are more plastic than closely compacted ones.
2. Aggregates of fine-grained kaolinites are more plastic than coarse-grained aggregates.
3. Flocculated aggregates are more plastic than deflocculated ones.
4. Flocculated aggregates are more plastic than cemented aggregates.

It would appear that, if these statements are correct, plasticity is a delicate balancing of two forces—one tending to hold the material rigid, and one allowing it to flow readily—the combination of the two giving a material capable of flowing when a sufficient pressure is applied to overcome the force tending to keep the mass rigid, the material breaking when this rigidity-force is wholly overcome. In this connection, it is interesting to note that J. W. Mellor has

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[1] *Bull. Amer. Cer. Soc.*, 1922, **1**, 153.

observed that when felspar, Cornish stone, or ground pottery is heated at 300° C. in compressed air so as to form a spongy mass with innumerable minute capillaries, and is afterwards mixed with water, a slight plasticity is developed, though curiously enough china clay and flint are unaffected by this treatment.

Since X-ray analyses of clays have revealed the structure of the typical clay-minerals, it appears to be highly probable that plasticity depends on the thickness of the films of water which can be retained between the solid particles, and possibly between the sheet-like molecular groupings which appear to form the lattice-structure of clay-minerals. If this is the case, plastic materials are those which can retain the largest amount (or the thickest film) of water between their units. Thus, in the structures shown in Table I. (p. 9) montmorillonite has the power of retaining so many molecules of water in the form of interstitial sheets as to increase the cell-thickness from 9·2 to 21·4 Ångstrom units, and it is easy to see that plasticity may be due to the ability of clays to absorb an even larger proportion of water between the sheets forming the crystal unit. The looseness of the association of these water particles gives free movements to those of the clay and so makes the mass plastic. If an excess of water is added some of it cannot be retained and the mass becomes sloppy or even fluid.

The retention of water may be greatly aided by the porosity of the material, as this would greatly increase the surface in contact with the water and surface-tension might then aid in increasing the water-content. Norton and Hodgdon[1] found the following to be the maximum thicknesses of water-films in clay pastes under a pressure of 100 lbs. per sq. in.—

	inches.	mm.
Milled quartz	0	0
Calcined china clay	0·0012	0·03
English china clay	0·0084	0·21
English ball clay	0·0096	0·24
Brick clay	0·0124	0·31
Bentonite	0·0132	0·33

Norton[2] has also found that there is a sudden increase in the "porosity" (water-absorption) of some plastic clays as soon as the water-content reaches a critical figure. At this point the normal pores are completely filled and any further increase in the water-content then separates the particles of clay by a film of water. Non-plastic materials do not show this phenomenon.

It has long been recognised that in a fully developed plastic paste (*i.e.* a paste in which the potential and actual plasticity are equal) the particles are completely separated by films of water. In this state the power of the clay particles to repel each other is equal to the power of the water particles to unite them into a solid mass. If more water is added, the mass breaks down and becomes fluid.

The plasticity-producing power of bentonite has been attributed to its rod-shaped particles; this shape is deduced from its streaming double refraction in suspension, which seems to indicate that its particles have colloidal dimensions in two directions and microscopic extension in one.[3]

Plasticity is also related to viscosity and, following Bingham, may be regarded as characterised by a critical pressure beyond which plastic materials behave like fluids. This view is supported by the behaviour of clays in presses

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[1] *J. Amer. Cer. Soc.*, 1932, **15**, 191.

[2] *J. Amer. Cer. Soc.*, 1933, **16**, 86.

[3] Bradfield and Zocher, *J. Soc. Chem. Ind.*, 1909, p. 506 A; Buzágh, *Koll. Zts.*, 1929, **47**, 223; *cf.* also Wherry, *Amer. Mineral.*, 1925, **10**, 65, 120.

and in extruding machines. If it is correct, plasticity may be expressed by $P=\frac{kv}{t(p-f)}$, where P is assumed to be the plasticity, k a constant, v the volume flowing in time t, p the applied pressure, and f the yield-value or pressure which must be applied before uniform flow occurs.

This equation shows P as the product of two factors: $\frac{v}{t}$, which is the rate of flow, and $\frac{1}{p-f}$, which is the reciprocal of the pressure required to maintain the flow after it has become uniform. Neither of these factors alone measures the plasticity, but it is possible that their product may do so. With fluids $f=0$, so that fluids have no plasticity.[1]

The chief objection to this view is that it does not give the same results as a practical clayworker when comparing different clays or the same clay with different " actual " plasticities (p. 108). Hall [2] has found that the results appear to be affected by some end-effect which becomes greater as the water-content is decreased, though its precise nature has not been determined. Some slippage of the clay in passing through the capillary also appears to occur, and this also affects the results. The steepness of the slope of a graph having the rate of flow as ordinates and the pressure as abscissæ is not proportional to the plasticity over all parts of the graph. Moreover, the position of the curve on the chart (*i.e.* in relation to the pressure) must also be taken into account.

Wilson and Hall [3] found that Bingham's method gives results comparable with the opinions of practical clayworkers if the paste is made with sufficient water to give it a viscosity of 0·3 poise. This involves a water-content of 50–60 per cent., which is much greater than that in ordinary clay-pastes, so that a strict comparison is impossible.

Plasticity depends, *inter alia,* on the water films, and one of the important factors controlling these is the quantity and nature of the exchangeable cations. The positive ions (H, Ca, Na, etc.) are arranged according to the electrolytes in the aqueous medium.

A certain rigidity in the water films is also due to the orientation of the water molecules.

The view that plasticity resembles some other characteristic properties of clay, such as shrinkage, strength on drying, etc., and is a function of the water-retaining power of the cations adsorbed on the surface of the molecular units forming clay (the so-called T-value [4]) seems to connect plasticity with both the physical nature and the chemical constitution of clays, because the T-value is closely related to the structure of the molecular complex and few substances have so high a T-value as clays. Unfortunately, commercial clays are of so complex a nature that the T-value alone cannot be used as a means of comparing plasticities.

That the chemical combination (if any) must be very slight is shown by the ease with which water is liberated from a plastic clay. Even on a slight pressure with the thumb or a pallette-knife water is visibly liberated, but is reabsorbed when the pressure is removed. Such ready " liberation " and " recombination " suggest a physical rather than a chemical cause of

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[1] See footnote (1) on p. 118.

[2] *U.S. Bur. Standards, Tech. Paper* 234.

[3] *J. Amer. Cer. Soc.*, 1922, **5**, 1916.

[4] The *T-value* is expressed by the number of milli-equivalents of cations per 100 g. of clay (the maximum value being 80–100). It corresponds to the total number of exchangeable ions in the clay.

plasticity. Osborne Reynolds has explained that when part of a wet mass of sand is compressed and the pressure is removed the compressed part appears to be drier, due to the displacement of the solid particles and a closer packing. If this occurred with clay it would lose its plasticity, so that in plastic clay the particles must not be packed too closely, *i.e.* they must have relatively thick layers of water between them. This suggests a physical origin for plasticity, but does not wholly exclude molecular attraction in retaining the thick film of water either between the particles or between the sheets of atoms in the crystal unit.

The fact that most (if not all) plastic substances contain a noteworthy proportion of colloidal matter has led to the suggestion that the latter is the chief cause of plasticity.

Hence, the causes of plasticity may be attributed to:

(*a*) The molecular structure of the clay-minerals.
(*b*) The colloidal matter in clays having a strong attraction for water.
(*c*) The surface attraction of the clay particles for water due to their physical structure.

That the *molecular structure* is the origin of plasticity has not been clearly established, though it is being increasingly recognised as the most probable.[1]

The *colloidal theory* is based on the facts that particles in the colloidal (gel) state have an exceptional power of retaining large quantities of water, and that a highly plastic mass resembles some colloidal gels in many respects.

The colloidal theory is considered on p. 124; it has many supports, but is by no means conclusive because it does not explain why other similar minerals are not as plastic as clays and cannot be made so, and in many highly plastic clays the proportion of colloidal material is too small for it to be the probable cause of their plasticity. The theory that the colloidal particles in clay are the chief cause of plasticity is not so popular now as formerly. It is increasingly recognised that the structure of clay-minerals revealed by X-ray analysis affords a much more satisfactory explanation. Plasticity is essentially a complex property of a nature which cannot be wholly attributed to the effect of a small proportion of colloidal matter mixed with a very large proportion of inert material.

The *physical structure theory* attributes plasticity to the small size of the particles and to their large internal surface (due to porosity).

If this theory is correct, plasticity is largely a mechanical factor due to the solid particles being able to slide over each other when subjected to a slight pressure, because they are suitably "lubricated" by a substance of appropriate viscosity. The "lubricant" may be a fluid,[2] or it may be composed of minute particles of a soft amorphous material, the former being

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[1] It is well explained in Houwinks' *Elasticity, Plasticity and Structure of Matter* (Cam. Univ. Press), 1937.

[2] Many substances which are plastic under certain conditions owe this property to the presence of a small proportion of bond or solid lubricant in an otherwise non-plastic material. This "bond" may be added, or it may be produced by heat and distributed by mechanical treatment. Thus, rolled zinc is often softer and more ductile than that which has not been rolled, and glass and many metals are plastic at suitable high temperatures. In the case of clays, the "lubricant" is generally a fluid—usually water, but occasionally oil or glycerine. In some branches of clayworking (such as pressing encaustic tiles) the "lubricant" is formed of the finest particles of clay, but a much greater pressure is then required to give the clay the desired shapes, as clay-dust is less efficient than a fluid "lubricant."

comparable to the oil, and the latter to the greases used in lubricating machinery. The nature and proportion of the "lubricant" to non-plastic matter must be such as to enable the particles to slide under slight pressure, yet to remain stationary when that pressure is removed. Hence, if too much "lubricant" is present, the particles will move too freely, and the mass will lose its shape, whilst, with insufficient lubricant, the material will not be plastic.

It is, therefore, necessary that the "lubricant" and other particles should have a high mutual attraction, and when given a "lubricant" (such as water) which produces different degrees of plasticity with various clays, it is obvious that the cause must be sought in the different chemical or physical constitution of the latter.

Most of the so-called non-plastic substances appear to consist of relatively small molecules of a dense nature, and it is difficult to obtain them sufficiently porous, so that the conditions of adequate "lubrication" or "wetting" are scarcely attainable. Clays and most colloidal substances, on the contrary, appear to consist of very large molecules, molecular aggregates, or complex arrangements with inter-atomic space-lattices. They include in their constitution a large number of atoms of the elements of water, and it is only natural to suppose that such substances should retain a large proportion of water on their surface, and so fulfil the mechanical conditions in which plasticity is possible. If this explanation is correct, it follows that the great difference between the plasticity of ball clays and china clays must be less of chemical than of physical constitution. Whilst plasticity thus appears to be a simple physical property, it is clearly dependent on a number of factors, and it is the failure to recognise this which has led to so many different theories as to the cause of plasticity. The chief of these factors are—

1. The nature of the molecules of the "true clay" present.

2. The extremely small size of the particles, their large surface (due to their porosity), and (possibly) their fissile character. The size and shape of the particles has a marked effect on the plasticity. Ruff and Riebeth[1] found the most favourable range in particle-size for clays is 0·0003–0·0025 mm., *i.e.* at the upper limit of colloidal dimensions. In the case of kaolins they found the upper limit to be 0·0036–0·0080 mm. It is well known that flaky particles develop more plasticity than spheres or cubes, and there is some evidence that rod-shaped particles do the same. According to Buzágh[2] only rod-shaped or laminar particles can form plastic masses of practical utility. It appears to be necessary to have not less than 20 per cent. of solid particles less than 0·0004 in. in diameter in a highly plastic mass. Substances containing too few minute particles are non-plastic.

3. The effect of water on the particles, and the probable production of inorganic colloid matter by its hydrolysing action on the clay, the amount of colloid material so produced being dependent upon the hydroxyl-ions present. If these are absent, or neutralised by hydrogen-ions, added purposely or occurring naturally or through fermentation of the organic matter in the clay, the plasticity will continue to increase until an excess of hydroxyl-ions is again produced; when the concentration of hydroxyl-ions is large, the negatively charged clay particles will go into suspension. As the extent to which water can be dissolved is very limited, the plasticity of clay can only be increased at so slow a rate that it is unlikely that very slightly plastic clays (kaolins) can ever be made highly plastic by artificial means, though the increase in plasticity may be sufficient to show the nature of the reactions which take place.

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[1] *Zts. anorg. allg. Chem.*, 1928, **173**, 385.

[2] *Colloid Systems*, London, 1937, 85.

4. The presence of organic colloid matter, due to impurities in the clay, or added purposely, may still further increase its plasticity.

5. The presence of minute quantities of soluble salts may exercise a pronounced effect on the plasticity. (Their action has been mentioned on p. 87.) The limits within which the plasticity of a clay can be increased by the addition of soluble salts are very small; but there is such an abundance of naturally plastic clays that it is only where materials of exceptional purity are required that an increase in plasticity is desirable. The *difference between plastic and non-plastic materials* is not wholly a matter of composition or grain-size or packing, but is a property of the surface of the plastic grains whereby they attract to themselves a stable film of water. This is the force which holds the particles together. It may be partly due to surface-tension, but is not wholly a physical phenomenon because it does not seem to be possible to make every solid substance plastic. There must be some affinity between the solid particles and the liquid. Dry solid clay gives plastic masses with water, the alcohols and some acids (lactic acid being specially effective), but not with hydrocarbons such as petroleum, benzene, etc., nor with amino- and nitro-compounds. It may be significant that almost the only liquids which produce plastic masses from clay are those containing active hydroxyl groups. The plasticity of different substances is not necessarily due to the same causes, and plasticity cannot be explained simply on structural chemical grounds because it is partly determined by the physical structure of the body.

Plasticity is the resultant of many factors, including the degree of dispersion, the type of subdivision, the kind of spatial distribution of the constituents (texture, internal structure), the composition of the dispersing fluid, viscosity, cohesion, absorption, adsorption, tensile strength, binding power, etc. It must, therefore, be considered in relation to these. This complexity makes the scientific study of plasticity a matter of great difficulty. Indeed, Planck[1] has shown that the property of deformability alone is determined by no less than 36 factors.[2]

An *increase in plasticity* may be obtained by any means which will increase the number of suitable ions or atoms in the aggregate or molecule, or which will reduce an extremely large aggregate to one of suitable size.

The following are the chief methods:—

1. By grinding or pugging the material with water and so increasing the amount and effectiveness of any "lubricant" by distributing it more uniformly. If the apparent lack of plasticity is due to insufficient water being present, this treatment will develop the latent plasticity but does not really increase the total plasticity. If the particles of clay are coarse or agglomerated, the combined action of the water and grinding may produce a sufficient proportion of extremely small particles to make the mass plastic. Commercial methods of grinding will not reduce the hardest and largest particles to a sufficiently small size to make them plastic, but will only tend to break down agglomerates of minute particles.

2. Increasing the number of hydrogen-ions in the material by allowing the organic matter in the clay to decompose (ferment) and become acid, or by adding a weak acid. The addition of an electrolyte (such as an acid) to clay is only of use in special cases where much of the colloidal material exists in the *sol state*, in which case the action of the electrolyte is to coagulate it, *i.e.* to convert it into the *gel state*, in which condition it can give plastic properties

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[1] *Mechanik deformierbarer Kōrper*, Leipzig, 1919.

[2] For further particulars and theories on plasticity see the author's *British Clays, Shales, and Sands* (Griffin), his *Chemistry and Physics of Clays and other Ceramic Materials* (Benn), or the Bibliography in *Ber. deut. ker. Ges.*, 1932, **13**, 408.

to the clay. The plasticity of some American fireclays has been greatly increased by the addition of 1 per cent. of hydrochloric acid, but others require the addition of an alkali. The addition of common salt sometimes has the same effect, but usually it reduces plasticity.

Endell has found that if the T-value, *i.e.* the cation-absorption capacity of a clay (p. 111) is only 3–5 milli-equivalents per 100 g. of clay the plasticity cannot be increased by chemical treatment, but only by adding one of the substances mentioned in paragraph 5 on p. 116. The addition of hydrogen peroxide increases the plasticity of some clays, but its cost is usually prohibitive.

3. By keeping the clay in intimate contact with water by stirring the two together. It is highly important to have the particles of clay as small as possible in order to facilitate the hydrolysis. If water alone is used for this purpose, the clay must be allowed to stand until fermentation of the organic matter sets in and the mass reacts faintly acid. In many cases, the time required for an appreciable increase in plasticity may be several years.

4. By keeping the moist clay paste in a cool, damp cellar so that any organic matter in it may ferment, producing weak acids which then coagulate any colloidal sol present. After prolonged storage, the paste must usually be well mixed by pugging.

The ancient practice of storing clay in cellars for a long time, known as *maturing* or *ageing*, is now seldom practised to anything like the extent which was formerly thought necessary. Where hollow goods of very fine clay are made there is an abundant advantage in thus storing the clay before it is made up into goods ; but the keeping of the clay in air-tight boxes for several years, as practised by Wedgwood and other famous potters, is no longer considered essential, though its beneficial effect on the clay is not denied. In Germany, the use of sumps, in which the clay and water remain in contact for a considerable time, is still regarded as necessary.

A much shorter storage of clay paste, frequently in open sheds, the material being covered with wet sacking, is known as *souring*. Its effect is undoubtedly to increase the plasticity of the clay, though there is a great variation in the extent to which it does this. The apparent effect of storing or souring is the formation of acid substances by the decomposition of the organic matter in the clays, and the coagulating effect of these acid-ions on the finest material in the clay. If this is the true explanation, it should be possible to reduce the time of storage by the addition of acid to the clay and then mixing it thoroughly. This treatment has proved successful in some cases, but not in all, probably because a certain amount of time is required before the whole of the mass can become permeated with the acid and water, and also because, in some cases, the plasticity of the clay may be at a maximum.

There is a widespread impression that souring is the result of bacteria or ferment organisms, and some potters have even added sugar or honey to the clay to assist the "fermentation." H. Spurrier found that the addition of hydrogen peroxide increased the evolution of carbon dioxide from a clay paste and facilitated the growth of algæ, the product becoming more plastic, from which he argues that the plasticity is partly a result of algæ growth. Whilst this may account for some of its effects, the hydrolysing action of the water present in the mass on the clay, silica, and iron oxide particles must not be overlooked. Rohland in 1903 suggested that the fresh clay paste is slightly alkaline, owing to the felspar, etc., present in the clay being hydrolysed and converted into a colloidal form. The acids produced by the decomposition of the organic matter also present neutralise the alkali-ions ; and the excess of hydrogen-ions produced coagulates the colloid matter and correspondingly increases the plasticity of the clay. Long previous to this, Seger had found that clays which remain alkaline do not increase in plasticity on storage, but do so if they are acidulated with acetic acid. This explains why the old vinegar " tip " of bygone potters, and the more modern use of peat extract (which contains humic acid) or tannin (which contains gallotannic acid), increases plasticity.

Some very interesting experiments by Acheson and Ries on the effect of a 2 per cent. solution of tannin (gallotannic acid) on clay show that the addition of this substance notably increases the plasticity of the clay, and at the same time apparently deflocculates it and breaks it up into much finer particles. The tensile strength of the clay was nearly doubled.

In a later patent Acheson first adds tannin and alkalies or ammonia and stirs the clay into a fluid state, and then by the addition of a suitable quantity of acid he coagulates the colloids and forms a stiff, plastic paste.

Rohland considers that heat is a disadvantage, and recommended that the souring should take place in a cool, moist cellar or shed if it is to be really effective; though in opposition to this, H. Spurrier[1] has found that if clay paste is stored at 80° F. to 90° F., its plasticity increases more than if the storage is at or below 60° F. It is also well known that slips which are dried by heat are often more plastic than those treated in a filter-press.

Some firms employ souring or storage for clays which are highly plastic, not to develop more plasticity, but to secure a better distribution of the moisture in the mass, and, as they express it, " to bring it to a better and tougher condition."

5. By the addition of a suitable bond, such as colloidal silica,[2] alumina, or iron hydrate, hot starch, dextrin, tannin, rubber, sumach, inulin, caramel, gelatine, gum, glycogen, or various ferments and enzymes, the plasticity of clay may be increased, but care must be taken to avoid confusion between true plasticity and the pseudo-plasticity caused by the addition of materials of an oily, gelatinous, or gummy nature. The use of flour paste and a stabilising agent (such as ammonia or soda) was patented in 1928 (Eng. Pat. 346,683), though the addition of an alkali usually reduces plasticity. The use of *aluminium soap* and of other soaps for increasing plasticity was patented in 1929 (Eng. Pat. 367,828).

6. The addition of bentonite[3] or an equivalent material differs from the methods previously mentioned because bentonite is often regarded as a clay-mineral though it is, of itself, devoid of plasticity. About 10 per cent. of bentonite when added to a slip of lean fireclay, mixed thoroughly and then stiffened on plaster to form a suitable paste, may yield a mass equal in plasticity to a good ball clay.[4]

An artificially prepared material with similar properties made by digesting halloysite with a small percentage of asphalt base oil is supplied by the Kraus Research Laboratory, Sparks, Maryland, U.S.A. The fact that the oil will burn away when the clay is heated in a kiln must not be overlooked.

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[1] *Journ. Amer. Cer. Soc.*, 1921, **4**, 113–118.

[2] The addition of gelatinous silica to clay was patented in 1882 by F. Render. For the use of other forms of silica used as bonds see Chapter III.

The addition of molasses, honey, water-glass, gum, and various adhesives is sometimes practised, but is of doubtful value. As an extreme case the mixture of 1 to 3 parts of molasses with 4 to 6 parts of fireclay, patented by I. Imray in 1883, may be noted.

[3] J. H. Beaumont, Eng. Pat. 224,257 (1923).

[4] *Cf.* P. E. Cox, *J. Amer. Cer. Soc.*, 1924, **7**, 151–153.

The addition of a highly plastic clay to a short or lean fireclay will also increase the plasticity of the latter.

7. Any method of purification (see p. 256) which increases the percentage of clay present will usually increase the plasticity.

8. Any mechanical treatment which increases the proportion of clay in a colloidal (gel) state tends to increase the plasticity, but is seldom practicable on a commercial scale as the cost of grinding in a colloidal mill is usually prohibitive (but see Eng. Pat. 193,520 of 1921).

9. A remarkable increase in plasticity results from *de-airing* the clay-paste, *i.e.* slicing it *in vacuo* and then pugging it under such conditions that no air can enter the mass. The proportion of air in clay-paste is so small that it is difficult to suppose that its removal is the sole cause of the increased workability.

The earliest English patent for de-airing *fireclays* appears to be 421,531 (1933), but it is void.

A problem which confronts many clayworkers, particularly those engaged in the manufacture of bricks and tiles, is how to keep the plasticity of a clay within convenient limits. So many clays, on drying, warp and crack to such an extent as to be very troublesome to the user, because the particles cannot move over each other with sufficient freedom, and have not sufficient rigidity to remain in their original position. Hence, it is necessary to reduce the plasticity of such clays in order to overcome these defects, and the correct adjustment of the plastic and non-plastic materials composing the clay mass requires the most careful attention.

To Reduce Plasticity.—Plasticity may be reduced, or even destroyed, by altering the chemical constitution of the material or by removing the "lubricant," as by drying the clay. The reduction may be either temporary or permanent.

The chief methods of reducing plasticity are—

(1) Hydroxyl-ions[1] may be added and the temperature raised (direct reduction). Any basic material, whether organic or inorganic, may be used, though lime-water is the cheapest.[2] If it is too weak in hydroxyl-ions, caustic-soda solutions may be used, as may any salt composed of a strong base and a weak acid, *e.g.* soda or potash or phosphates or silicates, which readily dissociate and liberate hydroxyl-ions, though the cathode constituent of the salt may exercise a considerable effect. Thus, borax reduces the influence of the hydroxyl-ions and potassium carbonate increases it, yet both are salts composed of a strong base and a weak acid. The concentration of the alkaline or basic material added is also of importance, and it may be necessary to render sulphates and other soluble salts insoluble by the addition of baryta, as suggested by Weber.

There are certain clays, as Weber has shown, in which the addition of an alkali increases the plasticity of the clay. This only occurs when clay has previously absorbed as much alkali as is required to deflocculate it completely, and the addition of an excess of alkali brings about a reverse reaction.

Certain clays containing organic acids of a fatty nature are saponified on treatment with alkali, and the soap so produced increases, instead of diminishing, the plasticity.

(2) The material may be heated to 200° C., or other suitable temperature,

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[1] Hydroxyl-ions are represented graphically by the symbol —OH. They are present in very dilute solutions of hydroxides such as caustic soda.

[2] See p. 125.

as described later. A comparatively small rise in temperature—produced by the action of mechanical stirrers—will reduce the plasticity of a clay if free hydroxyl-ions are present.

(3) The addition of non-plastic material (sand or grog) effects a reduction of the plasticity in an entirely different manner, by separating the clay particles from each other and enabling them to coat a larger number of particles, whilst at the same time " diluting " the clay. Such an addition reduces the strength of the material, but by diminishing the shrinkage it enables the clay to be used in a manner which would otherwise be impossible, and the strength is seldom reduced to such an extent as to make any notable difference to the user of the material. The proportion of non-plastic material to be added depends upon the size of its grains and on the binding power of the clay. As the latter is closely connected with its plasticity, it will usually be found that the more plastic the clay the larger the proportion of non-plastic material which may be used.

Some sands are quite useless for this purpose, so that great care is needed in their selection, and for refractory work, fireclay grog is always superior to sand.

To Restore Plasticity.—When the plasticity of a material has been lost, it can only be restored (*a*) by a fresh supply of " lubricant " properly distributed throughout the mass, or (*b*) by rebuilding the original constitution of the molecule or molecular aggregate. As an instance of the former, the addition of water to clay which has been dried, followed by a re-pugging of the mixture, may be mentioned. No means has yet been discovered for restoring the plasticity of a clay which has been heated to 700° C. or above, for such treatment destroys the constitution of the clay, and the synthesis of clay from its elements has not yet been fully accomplished (*cf.* p. 20).

The addition of bentonite or a highly plastic clay or of colloidal material (such as gum or glue), humus, peat or tannin may make a clay more workable, but does not increase the true plasticity. Sometimes, if a heated clay is ground very finely, some of the unaltered clay may be released and the plasticity of the whole may be thereby increased.

The Measurement of Plasticity has not been satisfactorily accomplished because the factors causing plasticity have not been accurately co-ordinated. Such measurements may be applied to (*a*) a material of which the " actual plasticity " is to be measured, or (*b*) a material which is first treated so as to produce the maximum plasticity or to develop as much of the latent plasticity as may be desirable. It is important to distinguish between these two materials; failure to do so often leads to confusion.

There are six chief methods used for measuring plasticity, though, strictly, they all measure some other property possibly related to plasticity:

(i) *Bingham's method,*[1] in which the plastic paste in a cylinder is forced through a capillary aperture; the rate of flow and the pressure are measured simultaneously and plotted on a chart.[2] The yield-value or pressure which must be applied before the clay-paste flows like a fluid is regarded as a measure of the plasticity (see p. 111). The lower the yield-value the more plastic is the clay; in a highly plastic clay the total deformability is also much greater than in a lean clay.

The method is vitiated by slipping of the clay and other experimental

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[1] Bingham, *Fluidity and Plasticity*, New York, 1922; Bingham and Green, *Proc. Amer. Soc. Test. Mat.*, 1909, **19**, ii, 640.

[2] A modification of Bingham's plastimeter which is more convenient for works' laboratories is described by Irwin and Bevis, *J. Amer. Cer. Soc.*, 1938, **21**, 66.

vagaries, but with many clays it yields comparable results, though not always in agreement with the plasticity as judged by practical clayworkers (see p. 108). A different interpretation of the results of Bingham's method due to Cassan and Jourdain[1] is worth noting. These investigators have found a definite relationship, namely $X \propto P$, where $X=\frac{\text{weight of water}}{\text{weight of clay}}$ and P is the pressure of compressed air applied to squeeze out the clay through a standard aperture 10 mm. in diameter. They regard X as proportional to the plasticity and state that all pastes of normal plasticity require the same pressure, 3·2 Kg./cm.². The quantity of water varies with the nature of the clay and so alters X. If, in a clay-paste, P is the pressure applied and $X=\frac{\text{volume of water}}{\text{volume of clay}}$, then $C=PX^b$, where C is the plasticity coefficient and b is a factor which depends on the water-requirement of the clay; it usually lies between 5 and 7, but is much greater for siliceous clays.

(ii) *Cameron and Lineberry's method*,[2] in which the apparent specific gravities of a clay mixture with varying proportions of water are plotted against the percentage of water in the mixture. The graph shows a sharp rise in the curve at a point which is regarded as a measure of the plasticity. This method is tedious and the results do not always agree with the plasticity as judged by practical clayworkers.

(iii) *Atterberg's method*,[3] in which the plasticity is measured as the difference between the proportion of water required to produce a mass at the " liquid limit " and that at the " plastic limit " of consistency. Atterberg defines the *liquid limit* as that at which the bottom of a cut in a pat of clay-paste in a dish just closes after ten light shocks on the hand have been given to the basin. The *plastic limit* is the lowest moisture-content at which the soil can be rolled with a thread $\frac{1}{8}$ in. diameter without the thread breaking in pieces. The *plastic index* (P) or Atterberg's Number is the difference between the liquid limit (l) and the plastic limit (p) or $P=l-p$.

In other words, Atterberg's Number indicates the proportion of water needed to convert a non-plastic mass in which the pores are filled with water into a mass to which rather more water has been added than is needed to produce the softest possible plastic paste.

If G is the percentage of non-plastic material, it has been found that, as an approximation:—

$P=0{\cdot}21\,G$ for diatomaceous earth;
$P=0{\cdot}15\,G$ for kaolin;
$P=3{\cdot}3\,G$ for bentonite;
$P=0{\cdot}3\text{–}3{\cdot}0\,G$ for plastic clays.

A modification of Atterberg's method consists in making a series of pastes by using different proportions of water, selecting the one which appears to have the most satisfactory consistency, weighing it, drying it, and then re-weighing it. The loss in weight calculated as a percentage of the weight of dry clay is then termed the *plasticity number*. With care it gives very consistent results in good agreement with the opinions expressed by practical potters on the relative plasticities of different clays, but it does not measure the actual plasticity and need not measure the potential plasticity.

(iv) *The penetration method*, in which the depth to which a weighted or other cylinder or ball sinks into the clay-paste, is regarded as a measure of the

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[1] *La Céramique*, 1937, **40**. 120.

[2] *Colloid Symposium Annual*, 1930, p. 179.

[3] *Int. Mitt. Bodenkunde*, 1911, **1**, 10–43.

plasticity. The results may be expressed in various ways. In one,[1] $d=at^p$, where d=penetration, t=time, p=plasticity, a=a constant differing with different clays. This method fails to include a time-factor which appears to be essential.

(v) *Pfefferkorn's method*,[2] in which a weighted piston falls on a standard cylinder of clay-paste; the original height divided by the height after compression (denoted by a) is (according to Pfefferkorn) proportional to the water in the mixture and to the plasticity. The " potential plasticity number " (Pfefferkorn) is the same as the percentage of water in a clay-paste in which $a=3{\cdot}3$ (this being an arbitrary figure). Some other investigators prefer to regard a as a measure of plasticity. For works tests, where only one series of clays, or various samples from the same or a limited number of seams are concerned, Pfefferkorn's method is convenient and reliable, but it measures deformation rather than plasticity, and Rieke and Sembach [3] have doubted the fundamental assumption that the plasticity is proportional to the water-content.

(vi) *Extensibility methods.*—There are several of these, among the earliest being that of Zschokke[4] followed by Rosenow and Jacoby, with later modifications by Hind and by Hyslop. Zschokke multiplies the tensile strength by the percentage of linear extension [5] of a cylinder 6 cm. high and 3 cm. in diameter. He made his test-pieces to a constant consistency, as judged by the " feel " and so ignored the water-content of the mixture. Rosenow and, later, Jacoby extended Zschokke's method by multiplying the percentage of linear extension by that of the water and dividing by the time multiplied by the tensile strength. Hind[6] prefers to determine the tensile strength rather than the compressive strength because in the former side-slips and other experimental vagaries are much reduced. He regards plasticity as one of several factors represented by the general equation $P=(M-M_0)^2\frac{L}{E}$, where P is the workability factor [7] (*i.e.* the way in which softness increases with an increase in moisture-content), M is the moisture-content, E the extension under the tension L, and M_0 a constant which gives the lower limit of plasticity for hand-working, *i.e.* the moisture-content at which the material ceases to exhibit plastic properties. It should be noted that the time-factor is included in M_0. Hyslop[8] plots the extensibility against the softness (*i.e.* the penetration) and obtains curves of the form $E=KS^n$, where E=extensibility, K is a constant, S=softness, and n is a measure of the plasticity. Care should be taken to distinguish between the actual and potential plasticity, as some methods measure the first and others the second of these properties. When determining potential plasticity it is essential to remove all occluded air or gases as these impair plasticity. The material should therefore be cut into small flakes and subjected to a vacuum (see *De-airing*) before the final compression in a pug-mill. No method yet published is wholly satisfactory,

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[1] Cf. *J. Amer. Cer. Soc.*, 1935, **18**, 352.

[2] *Sprech.*, 1924, **57**, 297; *Ber. deut. ker. Ges.*, 1934, **15**, 218.

[3] *Ber. deut. ker. Ges.*, 1925, **6**, 111.

[4] *Tonind. Ztg.*, 1905, **31**, 1658.

[5] The rate of extension must be rapid and constant, as low results are obtained by extending the clay-paste slowly.

[6] *Trans. Cer. Soc.*, 1930, **29**, 177–216.

[7] Hind considers that no single constant can be rightly termed "plasticity," and prefers "workability-factor" for P. He suggests that "there is a strong probability that P is a measure of plasticity."

[8] *British Clayworker*, 1936, p. 133.

though all those described give fairly constant results with a given clay. The great accuracy with which the tensile strength can be measured creates a predisposition in its favour, but the fact must not be overlooked that in practical usage the plasticity is associated with movement under pressure!

The plasticity of *dry clay* cannot be measured as it is not proportional to any single factor such as the tensile strength, but involves, as a factor, the water present in a plastic clay (see p. 109).

Plasticity at high temperatures must be distinguished from that of raw clays. It is usually " measured " in terms of the pressure and temperature at which the height of a cylinder is reduced to three-quarters of the original,[1] but a time-temperature graph gives much more information than any single figure.

The *workability* of a material is that property, or that combination of properties, which enables it to be used with a minimum of effort and results in the ease with which a clay-mixture can be shaped. There is no wholly satisfactory measure of workability, though it is so closely related to plasticity that the two are often confused. The best measure yet proposed is that of Hind,[2] who finds that it is related to two constants, B peculiar to the material and C to the rate of loading, so that B/C may be regarded as a softness-factor. Also, $B/C=\frac{\sqrt{E}}{L}$, so that the ratio B/C is in turn related to the factor M_0 in the equation on p. 120, the last being the lower limit of workability. The upper or " soft " limit of workability is indefinite.

Clays and clay-mixtures become workable when they contain a suitable water-content; the addition of further water merely makes them soften and increases their extensibility under tension.

The *binding power* of a clay is the property it possesses of uniting with non-plastic material and water to form a uniform plastic paste, and is consequently closely related to its plasticity. This absorption of non-plastic material by clay, with the spread of plasticity throughout the whole mass, has been attributed to the power of the saturated colloids (gels) to retain non-colloid particles in a state of pseudo-saturation. Other colloids are known to possess the power of preventing insoluble matter from settling, and this is, in some senses, a parallel case. Bischof has suggested that the binding power of a clay is a function of the cohesion and adhesion of its particles, but later investigators have questioned this, and have ascribed it to the presence of coagulated colloid matter. The author prefers to regard the nature of the clay particles as being the chief factor, those clays with highly porous molecules or specially numerous inter-atomic space-lattices having a greater binding power than others. Some writers appear to consider that binding power and plasticity are synonymous; this is by no means the case, as a clay may be very plastic and yet not be able to bind much non-plastic material into a uniform plastic paste. At the same time, there is clearly some relationship between these two properties of clay.

The binding power of a clay may be determined approximately by measuring the tensile strength of mixtures of the clay with various amounts of standard sand,[3] but a skilled clayworker can tell by the "feel" whether such mixtures are sufficiently strong to be useful. In order to determine how much lean clay or other non-plastic material can be added to a clay without unduly destroying its value for moulding into shape, Bischof's test may be

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[1] See "Refractoriness under Load" (later).

[2] *Trans. Cer. Soc.*, 1930, **29**, 177–216.

[3] The test must be made on wet material for the reason given later.

used. In this, the two materials are mixed in various proportions and the same measured quantity of water is added to each. The pastes are then rolled into small balls as equal in size as possible, and allowed to dry. They are then rubbed gently between the finger and thumb or with a small "camel-hair" brush. The mixture which just resists the action of the rubbing may be taken as the standard. Some authorities make up small balls of mixture in this way and then notice to what length a cylinder can be rolled from each without cracking.

Clays with a high binding power are known technically as "fat" clays; lean clays are deficient in binding power. Where highly refractory goods are to be produced, and have to withstand sudden changes in temperature, it is desirable to use clays with a high binding power (see *Binding Clays*, p. 39) in order that a larger proportion of grog may be employed.

The porosity of clay-pastes is seldom considered, but Norton[1] has found that the "porosity" of a plastic clay increases suddenly after a certain critical water-content has been reached. This is due to the additional water forming a series of films which separate the solid particles of clay.

The *tensile strength* of clay-pastes is considered by Hind and others to be closely related to the plasticity (p. 120) and the deformability (p. 123). According to Hind[2] it is in some clays equal to the square root of the *extensibility* E and the reciprocal of the softness-factor C/B (see p. 121), but this may not be a general relationship. It is important because of its influence on the tendency of some clays to crack during drying.

The tensile strength of the clay has, in fact, an important bearing on its resistance to accidents in the processes of manufacture, particularly from the commencement of the drying to the commencement of the firing. It is sometimes stated that the tensile strength of a clay enables it to carry a large quantity of non-plastic material, but this is rather confusing the effect with the cause. It is the binding power of a clay which enables it to carry such a large quantity of added material and still retain a sufficiently high tensile strength. Olschewsky has proved that there is no direct relationship between the binding power of a clay and its tensile strength when dry. It was at one time thought that the tensile strength of clays is proportional to their plasticity, but this is only true, if at all, when the pieces are tested in a moist (plastic) state. If air-dried, the definite relationship ceases.

The *strength* of dried clay is very important to those engaged in the manufacture of large, thin-walled articles. The factors which determine it are not all known, but they appear to be closely connected with the plasticity of the clay.

Ries and Orton have independently found that the non-plastic ingredients in clay influence its strength inversely as the diameter of their grains, so that fine-grained clays will usually be stronger, though an excess of either very fine or very coarse grains will weaken clay. In support of the theory that the grains of clay interlock to some extent, Ries has found that mixtures of two clays can be made which have a higher tensile strength than either clay taken separately. This fact has long been known by the makers of crucibles for melting steel in this country, as many as four different clays being used sometimes to produce a sufficiently strong crucible.

The *torsional strength*, or behaviour when subjected to a twisting force, has been investigated by Roberts and Cobb,[3] who found that it increased with the temperature at which the test-piece was fired.

[1] *J. Amer. Cer. Soc.*, 1933, **16**, 86.

[2] *Trans. Cer. Soc.*, 1930, **29**, 198.

[3] *Trans. Cer. Soc.*, 1933, **32**, 22; 1936, **35**, 183.

The *deformability*[1] of a clay is the force required to effect a definite alteration in its shape. As crushing tests are unsatisfactory, the deformability is usually understood to mean the percentage of extensibility, and is ascertained by placing a freshly moulded cylinder of clay (of such consistency that it will not adhere to the fingers, but is soft enough to receive delicate impressions) in a tensile testing machine and noticing its increase in length after fracture. Zschokke has found that more constant and higher results are obtained if the bar is stretched rapidly.

Ries prefers to determine deformability by noting the weight required to immerse a Vicat needle to a depth of 3 cms. in half a minute.

Ashley measures deformability by the air-shrinkage of the cast clay divided by the Jackson-Purdy surface factor, or the concentration of colloids multiplied by their specific air-shrinkage.[2]

The *cohesion* of clay is that property which counteracts the tendency to fall to pieces or to crack in drying, and so gives strength to the clay, both before and after firing. Any clay which lacks this quality is, therefore, liable to bring disaster to the user. Freedom from loss in manufacture is greatly dependent upon this property, and clays from different deposits vary considerably in this respect. It must be considered from two distinct points, viz. the capacity of the clay to resist tension and the power to resist a crushing strain.

The addition of non-plastic material to a clay materially reduces the cohesion of the whole, as measured by the loss in tensile strength and resistance to crushing; but although there are several explanations of the cause of this reduction, no general consensus of opinion has been reached, some authorities maintaining that it is due to the particles being prevented from interlocking, whilst others consider it is to be explained by the coagulated colloid matter being too widely distributed to bind the particles firmly together. Without rejecting these suggestions, the author considers that the power of the mixture to retain a "lubricant" is unduly weakened by the non-plastic material.

The *toughness* of clay in a plastic condition is also supposed by some to be due to the same cause as cohesion, but others refer it to the high binding power of the clay particles in the mass. Toughness is expressed scientifically in terms of: (1) *extensibility*, or the ability of the clay to stretch when pulled, which is measured by ascertaining the fullest extent to which a piece of given size will stretch without breaking; (2) *torsion*, or the extent to which a piece of clay can be twisted, which is measured by clamping one end of a bar rigidly and rotating the other slowly by means of a screw and counting the number of complete revolutions which can be made before the bar breaks; (3) *bending moment*, or the angle through which a bar of clay of given size can be bent without rupture; (4) *elasticity*, or the extent to which a piece of clay can be stretched and yet return to its original length when the tension is removed. Many plastic clays show slight elasticity, though it is usually too small to be measurable.

Adsorption is the power possessed by certain substances of removing other dissolved substances from solution. Thus, if a plastic clay is thoroughly mixed with a solution of dye-stuff and allowed to settle, it will remove the dye-stuff from the solution, and will deposit it on its own surface. If a salt solution be treated similarly, it will be much weakened by the salt adsorbed by the clay particles. In neither case can the adsorbed dye or salt be removed by washing the clay.

[1] Sometimes termed the *consistency*.

[2] The method is described in *British Clays, Shales, and Sands*, p. 331.

Care must be taken to avoid confusion between the terms "absorption" and "adsorption." The latter relates exclusively to the withdrawal of the dissolved substances from solution and the retention of them on the surface of the solid particles.[1] The same power is possessed by charcoal and filter-paper in a very high degree, and is attributed to their colloidal nature. The amount of substance which can be adsorbed is apparently proportional to the surface area of the solid substance, and is a function of the nature of the solid and dissolved bodies and of the concentration of the latter.

Both *ab-* and *ad*-sorptive powers are important in fireclays, as they explain how the latter are made more fusible when placed in contact with salt solutions. They also have an important influence on the plasticity of the clay, as adsorption is a characteristic of colloids (gels) and also of plastic clays, and it has been suggested by several investigators that the plasticity of clay may be due to its adsorptive power, but it is doubtful whether this explains the whole of the plasticity.

Semi-permeability is a property possessed by plastic clays and some colloidal gels, these substances being thus named because they are permeable to some substances and not to others. Thus, a diaphragm made of certain plastic clays will effect a perfect separation of a soluble from a colloidal material as the former rapidly diffuses through the diaphragm, whilst the colloids are retained, except in some cases, *e.g.* a mixture of sodium chloride and colloidal silicic acid, where a soluble salt aids the passage of a colloid. Again, if certain mixtures of colloidal and soluble matter are stirred up with a suitable plastic clay, the truly soluble matter will be adsorbed by the clay, and the liquid after filtration will contain only the colloid. In this way, it is possible to effect a complete separation of sugar and tannin in a mixture; the dissolved sugar is adsorbed whilst the tannin, being a typical colloid, remains in suspension. There are exceptions to this rule, *e.g.* certain colours, such as aniline dyes and some animal, vegetable, and tar colours, which are truly soluble and yet are retained by plastic clays. Thus, some clays certainly appear to be composed of granular matter covered with colloidal gels derived from organic matter such as peat or from colloidal silicates, silica, and more rarely from alumina and iron oxide. The presence of the granular matter is important, though its influence appears to have been overlooked by some writers.

It may be desirable to explain here that many solid substances may exist in either of two forms: (*a*) *soluble*,[2] in which case the particles can be deposited from a solution in crystals of regular form and possessing definite and constant shapes; and (*b*) *colloid*, in which the particles are so minute that though they appear to be in solution they are really in suspension. Solutions of truly soluble substances have a high boiling-point; the substances themselves have a comparatively low molecular weight, and only a definite amount can enter into solution; but colloid solutions have only a slightly supernormal boiling-point; the substances have an indefinite but very high molecular weight and no distinct solubility coefficient. Most colloid solutions are easily coagulated either by heating or by the addition of an electrolyte.

Colloids usually differ from truly soluble substances in being soft and

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[1] It is often extremely difficult to ascertain whether certain properties of clays are due to their *ad-* or *ab*-sorbent powers; the latter are chiefly concerned in most cases.

[2] The term *crystalloid*, which was proposed by Graham to distinguish dissolved substances from those in the colloidal state, is no longer correct, as some colloidal substances are definitely known to be composed of minute crystals.

irregular in form, with only a weak power of combining with water, though they absorb it readily.

Colloids exist in two forms: (*a*) in suspension in a liquid in which they mostly behave like solutions, and are termed *sols* or *hydrosols*;[1] and (*b*) as a jelly whose pores are filled with a liquid, termed a *gel* or *hydrogel*. If they can turn from the sol to the gel state and back again, they are termed "reversible"; but gels which cannot be converted into sols are "irreversible." The process of passing from sol to gel is termed "coagulation"; the reverse process is "deflocculation." If a gel cannot be converted into a sol it is said to be "set," and any process which effects this is termed "setting." The cause of this coagulation is still in dispute. Rohland believes it to be due to the direct action of electrolytes, particularly those which on dissociation produce hydrogen-ions, the reverse action, *i.e.* the formation of a clay-suspension (sol), being due to an increase in the opposite particles, amongst which hydroxyl-ions are the most important, as in the case of water. According to Sven Odén,[2] the particles of clay, on coagulation by electrolytes, retain their individual character and merely adhere to each other, the speed of flocculation and the size of the aggregates depending upon the varying sizes and charges of the particles. On shaking such a deposit, the particles are deflocculated, even in the presence of a flocculating agent, but, when the shaking ceases, flocculation again takes place at a definite speed as before. He considers that when particles of clay are flocculated, they are held together by a film of water surrounding each particle. Particles connected in this manner can be separated by shaking, but if the shock of contact breaks the watery film and the particles come into direct contact the process is irreversible.

Thus, the presence of hydroxyl-ions favours the formation of colloidal solutions, whilst hydrogen-ions act contrarily. This is due to the fact that particles of colloid matter in suspension acquire an electric charge which is positive or negative to that of the liquid, the metallic hydroxide colloids being charged positively with respect to water and others negatively.[3]

Clays, like colloids, are very sensitive to the action of electrolytes, a few drops of a solution of caustic soda or barium hydroxide making a stiff clay paste into a fluid. It becomes stiff again on the addition of sufficient acid to neutralise the alkali present. This corresponds very closely to the action on electrolytes or the coagulation and re-suspension (sol formation) of colloids.

G. A. Bole[4] considers that the plasticity of clay is caused by the films of colloidal matter having a polarity opposite to that of the grains of non-colloidal matter, which they enclose, and that the addition of a deflocculant electrolyte causes the attraction of the outer portion of the film to ions of the same polarity as the clay grains, and, consequently, reduces the thickness of the film, so that particles before in contact now repel each other, on account of like polarity. Flocculation acts in the opposite direction by increasing the thickness of the film of colloidal matter.

Plastic clays behave in a manner so similar to colloid substances that some investigators think they contain colloidal matter to a very important extent, though the proportion of it varies greatly.

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[1] When a colloidal sol is examined by means of an ultramicroscope, it will be seen to consist of countless tiny particles in a state of violent oscillation. This oscillation—termed the "Brownian movement," after its discoverer—may be observed in all clay-suspensions, though the finer clays show it much more strongly than others.

[2] *Journ. Landwirtschaft*, 1919, **3**, 177.

[3] This is the usual explanation, but it does not show what chemical changes (if any) occur in the constitution of the colloid.

[4] *Journ. Amer. Cer. Soc.*, 1922, **5**, 469.

Expansion.—When water is added to a dry clay it is first absorbed in the pores, but when these are filled any further supply of water appears to cause a separation of the particles from each other, so that the volume of the clay is increased, though not in proportion to the water added. The amount of water which can be absorbed in this manner varies greatly with different clays. That which is absorbed in converting the clay into a good modelling paste is termed "water of formation." It reaches a limit beyond which the pasty mass loses its shape and begins to behave like a thick fluid, so that the stage at which the clay contains a maximum quantity of water of formation is also the point of maximum plasticity.[1]

If by any means some of this water is removed, the volume of the mass begins to diminish and contraction occurs.

A second expansion occurs when clays rich in silica or silicates are heated to 800° C. or above. This is due to the fact that those forms of silica which are stable at high temperatures have larger specific volumes than those stable when cold, and that most crystalline solids (including mica and felspar) expand on fusion. This expansion is usually obscured by the much greater contraction which occurs during the drying and earlier stages of burning.

Contraction or *shrinkage* is chiefly, but not entirely, due to the removal of water from clay by evaporation at the ordinary temperature (air-shrinkage), at a somewhat higher temperature in a dryer (dryer-shrinkage), or during the burning (kiln- or fire-shrinkage). The use of acid water reduces shrinkage; alkaline water often increases it.

As all coagulated colloids (gels) which are saturated with water shrink when the water is removed, some investigators consider that the shrinkage of clay may be due in part to this cause. The more general idea (which states facts rather than explains them) is that, as the water is removed, any which remains draws the clay particles, by means of its surface tension, into a smaller and denser mass.

If, during the drying, the clay is not subjected to draughts, the contraction will take place equally in all directions, and the shape of the articles will be retained. Highly plastic clays shrink irregularly and set up internal strains which may easily cause the articles to crack.

The amount of shrinkage appears to depend upon the rate at which the clay is dried, for if this operation is performed rapidly, the shrinkage will be less, the clay particles not having time to move over each other so freely as when the drying is slower. Rapid drying tends to crack dense clays, owing to the particles near the outer surfaces contracting more than those near the centre of the article. Hence, it is necessary to determine the best conditions of drying a given clay. When drying a fireclay, the water at first evaporates from the surface and is replaced by capillary action from the interior, the mass contracting by the same amount as the water diminishes. All the pores remain filled with water until the rate of evaporation exceeds the rate at which the pores transmit water. This point occurs when the clay particles move so much less freely on each other that the rate of evaporation begins to exceed the rate of contraction. After the first stage of surface drying, the exterior of the mass loses water more rapidly than the interior; in the second stage now reached, the pores are no longer filled with water at their outer ends, and begin to form spaces in the clay, filled with air and vapour. Contraction still occurs throughout this second stage until the substance of the clay is so far solidified that the individual particles can no longer slip on each other at all.

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[1] Some physicists regard this stage as the saturation-point of the coagulated colloids (gels) in the clay. Such *swelling* is a characteristic of colloidal materials.

The third stage is then reached, in which capillary attraction and shrinkage cease entirely. Evaporation now takes place entirely inside the mass, and spaces are formed exactly corresponding with the volume of water lost.

If the water is irregularly distributed, or one part of the clay dries more rapidly than another, the clay will twist or crack on account of the internal strains caused by irregular shrinkage. This is particularly the case if the outer surface of the clay becomes dry and hard whilst the interior is still wet, and if the clay is heated to such a temperature that the steam produced within the mass cannot escape with sufficient rapidity.

Fire- or kiln-shrinkage occurs when part of the ingredients commences to fuse. The liquid, then produced, draws the solid particles closer together and occupies the pores. Fire-shrinkage is partially compensated by the expansions which occur when the crystalline silicates present begin to fuse, and when the transformation of flint or quartz into other forms of silica occurs, with the result that the total reduction in the volume of the goods, whilst in the kiln, is usually very small.

It should be noted that the shrinkage is usually greater with fine particles than coarser ones.

The *homogeneity*, or uniformity of physical composition of mixtures of clay and water, is an important characteristic, for unless the material is of the same nature throughout it will be very difficult to obtain satisfactory results. For this reason, clayworkers endeavour, by means of crushing and mixing plant of various forms, to temper, pug, or mix the material. For small amounts of clay, *wedging* or mixing by hand may be employed, but for larger quantities mechanical mixing appliances are essential. Those most frequently used are pan mills, pug mills, and blungers, according as the clay is coarse, fine, or to be mixed in the form of a slip. The mixture will be more uniform if the clay has been previously weathered, ground, and dried.

Perfect uniformity of composition is seldom, if ever, secured, but by fine grinding, followed by repeated pugging, with intervals of rest to permit the water to penetrate the mass completely, a sufficiently uniform mixture may usually be obtained.

The Effects of Heat on the Characteristics of Clay.—When moist clays are warmed gently, the chief effect of the heat is to drive off the moisture and so dry the clay. This can only be accomplished in the presence of a quantity of air sufficient to absorb the moisture thus vaporised, so that wet clays heated in closed vessels or chambers do not dry appreciably. The rate at which a clay can be safely dried depends upon the size and shape of the mass, the amount of water it contains, the quantity of colloid present, the power of adhesion possessed by the particles, and the porosity of the material. Clays may contain, without any special appearance of wetness, as much as 30 per cent. of evaporable moisture, the maximum amount depending on their porosity, and on the amount of hydrated silica, iron oxide, carbonaceous matter, and other active colloids present. When this moisture is removed, if the exterior parts lose water more quickly than the interior, the clay must be submitted to some internal strain, which must not exceed the adhesive power of the particles, or cracks will be formed.

The removal of the moisture is accompanied by a reduction in the volume of the clay mass (see *Shrinkage*) and a temporary loss of plasticity. Both these can, however, be restored on adding water to the clay, provided that the temperature to which the material has been heated is not sufficient to convert any colloids present into irreversible gels or otherwise to destroy the constitutional structure of the clay.

When a clay which has been mixed with water is left in a hot atmosphere the water evaporates progressively. As long as the body preserves a sufficient plasticity, the departure of the water results in the grains of clay coming closer together in proportion to the volume of water removed; but when there is no longer sufficient water to allow the grains to become displaced, the shrinkage ceases and the evaporation of the last portions of water causes the formation of pores in the interior of the mass.

The dry body thus obtained no longer resembles the original clay; it forms a harder mass of a greater density, and the molecular attraction continues to be so powerful after the departure of water that, unlike other (non-plastic) mineral powders, it retains its form and does not fall into powder when dried.

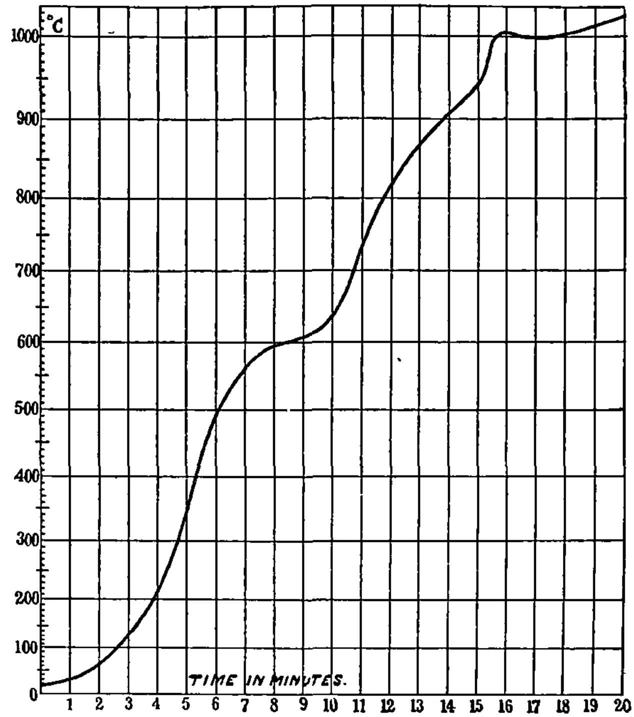

FIG. 20.—Heating curve of Derby fireclay.

If the temperature of the clay is increased considerably, many notable changes in its characteristics will occur, and some new ones will be observed. For example, the clay will gradually lose its softness, sectility, and plasticity, and will become hard and stone-like. It also loses what is known as its "combined water," viz. that which is an integral part of the clay molecule. The evolution of this water is, apparently, accompanied by a decomposition of the clay, though the approximate composition of the residue is not fully proved. If the changes in the temperature of the clay are recorded when the temperature of the furnace or test-kiln is kept constant, they will be found to show two marked points at which internal changes occur. These two points —

one between 500° C. and 650° C.,[1] and the other at about 800° C.—are clearly shown in figs. 20 to 22, which are reproductions of graphs obtained by H. Brearley in 1897. It is important to observe how closely these curves resemble each other notwithstanding the great differences in the chemical composition of the clays, as shown by analysis.

Houldsworth and Cobb [2] found that fireclays and ball clays show an additional critical range from 80° C. to 160° C., which they regard as due to the loss of water from the colloid matter present. This range does not occur in china clay.

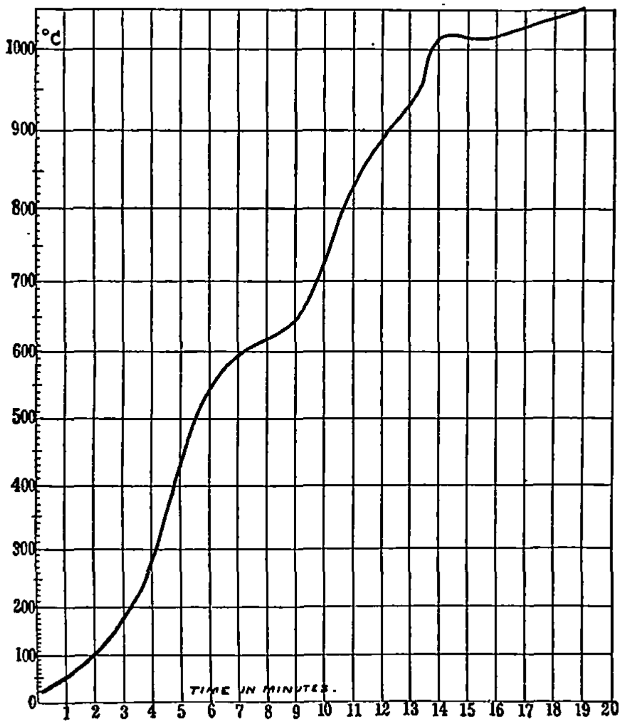

Fig. 21.—Heating curve of Stourbridge fireclay.

As explained on p. 30, it is generally agreed that all clays are decomposed at 500° C. to 650° C., with the evolution of water, but it is not yet settled whether the residue consists of a mixture of free alumina and free silica or of an anhydride, or if all these substances are present.

If the heating is continued to a temperature above that just mentioned as required to decompose the clay, the felspar, mica, and other minerals present may exercise a fluxing action and produce vitrification. The effect of various fluxes has been described on pp. 67-101; their total effect is to produce a glassy

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[1] The temperature at which the decomposition commences is considerably lower than 500° C., and may occur with extreme slowness at almost any temperature above that of the atmosphere. It is barely appreciable at 300° C., but at 500° C. and above the decomposition is very rapid.

[2] *Trans. Eng. Cer. Soc.*, 1922-23, **22**, 111.

mass which, if sufficient is produced, fills the pores of the material and produces a vitrified and impervious body. In the case of fireclays, the proportion of fluxes present is quite small, so that, if well distributed, they act chiefly as a binding agent, uniting the particles firmly together and yet leaving a porous mass.

The amount of glassy material produced, and its distribution through the whole mass, depends on a number of conditions, the chief of which are the nature of the fluxes and the sizes of the particles of clay and fluxes. If the particles are small, they react gently on each other at a moderate temperature and soon produce a considerable amount of glassy matter, and the more fluid this molten material, the greater will be the corrosive effect on the residual clay. Some silicates are very viscous when just molten, and do not flow into the interstices so readily as the more fluid material, and cannot, therefore, exert such a great influence on the clay. Thus, as stated previously, lime is a very active flux, and its compounds with clay and silica, when molten, are particularly fluid, whereas magnesia produces a very viscous liquid and exerts a far less severe action. Consequently, on heating a mixture of clay and flux, or an impure clay, there is produced a heterogeneous material consisting of a porous mass of amorphous particles, frequently termed the *skeleton* or *sponge*, and a glassy matrix which fills some or all of the interstices in the former. In the case of a fireclay, the proportion of sponge is very large and that of the matrix very small, whereas in hard-paste porcelain—which is also a refractory

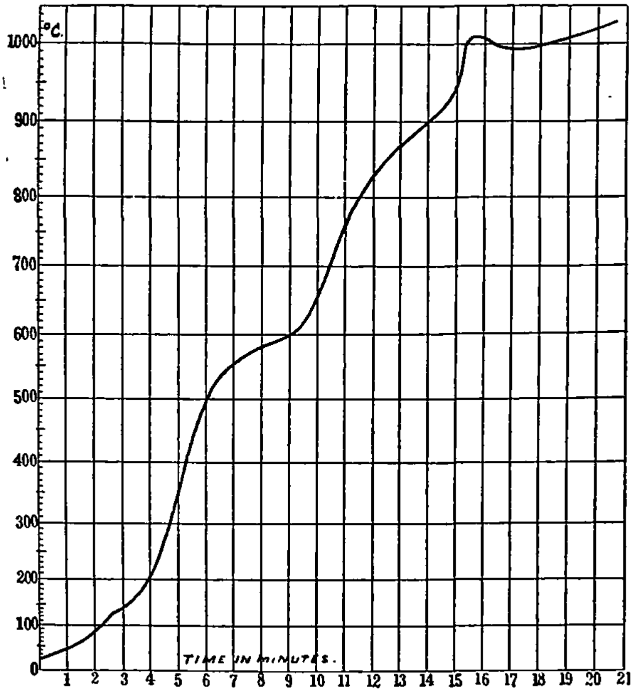

FIG. 22.—Heating curve of Stannington fireclay.

material—the proportion of glassy matter is sufficient to completely fill all the pores in the skeleton.

The formation of this fused glassy matter does not proceed regularly, but depends on the melting-points of the various silicates, etc., formed by the action of the impurities present in the clay. Consequently, at some part of the heating, a comparatively small rise in temperature may be accompanied by a great increase in the amount of molten material produced. When the clay reaches a temperature of about 1250° C., and still more rapidly at 1400° C., if the proportion of molten matter is not too large, the conversion of the material into mullite ($3Al_2O_3.2SiO_2$) occurs. The conversion is rendered more rapid by the presence of certain impurities, which act as catalysts and aid in the dissociation of clay. The most important catalysts are iron and fluorspar (or cryolite). Bauxite or other aluminous material may also be employed to combine with any surplus silica and so form mullite. On cooling, this compound crystallises in the form of minute laths or rods with characteristic square edges, which form a felted mass. The evolution of heat shown in figs. 20–22 appears to be due to the crystallisation of the free alumina.

Owing to the different reactions just mentioned, the conversion of quartz into tridymite, the polymerisation of any free alumina, etc., a clay or clay mixture, when sufficiently heated, undergoes various changes in volume, and at a sufficiently high temperature it will begin to lose its shape, and may (if impure) fuse to a shapeless mass. This latter is practically impossible with a pure fireclay on account of its great refractoriness. When heated steadily with the temperature rising gradually at the rate of 10° C. per minute, the purest fireclays will soften sufficiently to lose their shape at 1770° C., but complete fusion will not occur until a much higher temperature is reached, and the perfect fusion of such clays is unattainable except in the electric arc. When firing articles made of clay, it is of course necessary to arrest the burning before a temperature is reached at which they lose their shape.

When a clay is heated strongly it does not behave like a single element or compound such as iron, silver, or ice, which has a definite melting-point, but as a mixture of various substances, each of which commences to melt at a different temperature, so that it becomes increasingly fluid as the temperature rises. Thus, if a piece of fireclay is slowly heated, it will lose water and decompose, but it will not show a definite melting-point, and, except for several small variations owing to compounds present being decomposed and new ones being formed, the temperature in a commercial kiln may be raised steadily the whole time. The various changes which occur can be shown on an experimental scale on curves similar to figs. 20–22, each change in the direction indicating a decomposition or the formation of a new compound (see pp. 30, 31). Simultaneously various reductions or increases in volume occur (see " Shrinkage," p. 126).

If the heating is carried beyond commercial usage, so that fusion occurs, the first liquid to form (with pure clay) is the eutectic composed of 94·5 per cent. of silica and 4·5 per cent. of mullite. If the heating is sufficiently prolonged, alumina and silica will be dissolved and on cooling mullite ($3Al_2O_3.2SiO_2$) will crystallise out in long flat bars, which usually form a felted mass. If complete equilibrium is obtained and the clay is perfectly pure, the final product will consist of 64 per cent. of mullite and 36 per cent. of free silica (cristobalite). If the temperature is raised above 1810° C., the mullite will partially decompose and form a mixture of corundum (Al_2O_3) and mullite.

Unfortunately, perfectly pure clay is seldom, if ever, obtained and a much more complex mixture is produced, an important part of which is the glassy mass containing all the impurities, chiefly in combination with silica or alumina or both—and melting at a temperature between 800° C. and 1500° C., according to its composition.

In the heating of a fireclay, therefore, four distinct stages may be noted, though some of these may occur simultaneously—

1. *Baking* or heating until the clay is decomposed and no further loss of water occurs. At the end of the baking period the clay forms a moderately hard, porous mass.

2. *Vitrifying* or heating until some of the ingredients have fused or partially filled the pores. With good fireclays very little vitrification can occur at temperatures attained in industrial furnaces, but with the more fusible ball clays and stoneware clays the whole of the pores may become filled with fused material. The greater the proportion of vitrified material present, the stronger will be the *cold* article made of burned clay, but the weaker will it be when at a high temperature.

3. *Squatting* or *softening*, which occurs when so much of the material has fused that the mass begins to lose its shape and becomes viscous.

The temperature differences at which these changes occur vary with each clay; thus, a clay rich in magnesia may be far more completely vitrified without losing shape than another clay containing the equivalent proportion of lime. Hence, the influence of the impurities in a clay is often most powerful when the latter is heated to the temperature of vitrification of the mixture.

The difference between the sintering-point or commencement of vitrification, and that at which loss of shape occurs,[1] is very small (about 30° C.) with calcareous clays, but with fireclays and some ball clays it is at least six times as much (200° C.). The difference is greatly reduced by pressure.

4. *Fusion* occurs if the material is changed from the solid to the liquid state, but complete liquefaction takes place so gradually with most clays that a " fusion-range " and not a " fusion-point " is obtained.

Fusion may commence at a temperature of only 900° C., but may be incomplete after the material has been heated to a temperature of 1900° C., though the amount of fused substance has increased all the time.

As their name implies, fireclays are so resistant to heat that they seldom fuse completely when heated alone, but in contact with bases such as lime, ashes, etc., they fuse readily, as the bases combine with the clay and form fusible silicates, aluminates, and alumino-silicates.

C. W. Kanolt found that, in 41 samples of American firebricks, sufficient fusion occurred to cause a visible flow at 1555° C. to 1725° C., with an average of 1649° C. No data have been published on the total fusion of British fireclays, but the temperatures at which they soften and bend lie between those mentioned by Kanolt.

The *fusibility* of fireclays is increased, and their refractoriness correspondingly lowered, by the addition of free silica or a silica compound (except burned clay of equal or greater refractoriness), and all compounds containing metallic oxides. The only exception to this is alumina, the addition of which makes a clay more heat-resisting. In other words, any impurity in a fireclay will make it more fusible. The nature, proportions, and size of the grains of the particles constituting the " impurity " are all important factors in determining how much fusion will occur and under what conditions the clay will lose its shape.

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[1] This is sometimes known as "the range of vitrification."

To reduce the fusibility of a clay and neutralise part of the effect of any fluxes it may contain, the material should be diluted with another refractory clay which is low in fluxes, or with a pure sand. The dilution reduces the percentage of fluxes, and so increases the refractoriness of the clay. If no addition of clay or sand is practicable, the clay should be used as coarsely as possible, as fine grinding increases the speed at which the fluxes react with clay.

As fireclays are seldom heated to fusion, it is more convenient to consider their fusibility under *Refractoriness.*

Fused clay may be made by heating a calcined clay in an electric arc. The softening- and melting-points are not altered, but the density is greatly increased and the resistance to corrosion is enhanced. The molten clay may be run into moulds, and in this manner bricks or other articles are produced.

Vitrification is a term used to indicate the filling of some or all of the pores by fused material. The amount of fused or vitrified matter so produced has an important influence on the properties of the product. Whilst *hot,* a large amount of vitrified matter will make the material semi-fluid; after cooling, the (solid) vitrified mass will be far stronger and less pervious to water than a more porous one.

In a material which is required to be refractory, the presence of such vitrifiable matter is detrimental, but where strength and impermeability is of importance, a large proportion of vitrified material is desirable. The amount of vitrification which occurs at any given temperature and under any given conditions of heating depends on the amount of fluxing materials present in the clay and on their nature. Felspar begins to show signs of vitrification at 1190° C., but it is not completely fused below 1300° C.; though, if mixed with clay and chalk, a material becoming quite fluid at 1200° C. may be obtained. Chalk alone, as already mentioned, is almost infusible, but it may combine with clay to produce a material which fuses at 950° C. It is, however, very difficult to ascertain the precise temperature at which vitrification begins, as a certain amount of material must be fused before the difference in the porosity of the ware can be noticed. As the temperature rises, the rate at which the fused material is produced increases very rapidly.

The rate at which vitrification occurs is also important. For binding purposes, it should occur slowly at a moderate temperature, but more refractory materials should vitrify very slowly indeed, and only at a high temperature.

The *refractoriness* (or resistance to fusion) of fireclays has been defined as their power to resist the action of heat under a steadily rising temperature and in the absence of disturbing conditions. There is a tendency in some quarters to overlook the fact that whilst flue-gases, fluxes, and other agencies may affect the heat-resisting power of a clay, they do not alter its true refractoriness. For this reason, it is not sufficient to judge refractory clays by the refractoriness alone. Many clays which can withstand a very high temperature when heated under laboratory conditions prove to be useless in works' furnaces, and any test of the refractoriness of a clay is, therefore, chiefly of value in distinguishing it from non-refractory ones rather than in showing its commercial value as compared with other similar clays.

Clays vary greatly in their refractoriness, some very calcareous marls fusing at a red heat, whilst high-grade fireclays and china clays have a softening-point above 1700° C.

For convenience, it is customary to recognise three grades of fireclay articles, No. 1 grade consisting of the most refractory goods, the clays concerned softening at temperatures equivalent to Seger Cones 35 to 36 ; No. 2 grade softening at temperatures corresponding to Seger Cones 30 to 35; and No. 3 grade corresponding to Cones 26 to 30.[1]

The refractoriness of a clay is a function of the time of heating as well as of the temperature. If a clay is heated for several days, it will soften and lose its shape at a temperature of 100° C. or more below that which must be reached if the heating is to be only of a few hours' duration. The difference appears to be wholly due to the time taken before the whole of the material is at a specified temperature. The thermal conductivity of some firebricks is so low that one side may be at a bright red heat, whilst the opposite side only feels " comfortably warm."

The refractoriness of a firebrick or block is greatly reduced if the article is under pressure. Thus, Bleininger and Brown have proposed to compare firebricks and refractory clays by applying to them a pressure of 50 lbs. per square inch, raising their temperature to 1350° C., and maintaining it at that temperature for an hour. A No. 1 grade brick under this treatment will not show any obvious change of shape, and will not shrink more than 11 per cent. in the direction in which the pressure is applied.

The plasticity of a clay does not appear to bear any direct relation to its refractoriness, though the more plastic clays resist the action of fluxes better than those which burn to a more open body.

The texture of a clay is important, as the smaller the particles the more easily will the clay fuse, as they enter more quickly into reaction with the fluxes than do the coarser particles. The use of reducing gases in a furnace in which clay is heated will also make it more fusible, as the iron oxide present is reduced to ferrous oxide, which rapidly attacks the clay, forming a fusible slag.

The refractoriness of a clay is usually tested by forming it into small tetrahedrons of the same shape as Seger cones, but about half the size of those used in ordinary kilns. Special Seger cones of this size may be purchased as standards for testing.

Refractoriness and Composition.—Many attempts have been made to find a definite relationship between the refractoriness of clays and their composition, but these have been unsuccessful except with the purer clays.

Although the refractoriness of a clay is, to a certain extent, dependent on its composition, it does not at present seem possible to obtain any " factor " which can adequately represent its power in this respect and be deduced from the analysis of the clay. Bischof and Seger both suggested factors of this kind, and although both are accurate within certain narrow limits, they are not, on the whole, satisfactory.

Bertrand[2] compared the percentage of alumina with the refractoriness in a hundred different clays, and found that—

1. All the clays with more than 29 per cent. of alumina had a softening-point above 1650° C.
2. Fifty-three clays contained 20 to 28·9 per cent. of alumina; of these, thirty-nine softened at temperatures above 1650° C., whilst fourteen softened between 1120° and 1650° C.

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[1] The Institution of Gas Engineers' (1934) Standard Specification recognises:—

No. 1 grade showing no signs of fusion when angular pieces are heated to not less than Seger Cone 29 (about 1650° C.).

No. 2 grade showing no signs of fusion when angular pieces are heated to not less than Seger Cone 26 (about 1580° C.).

"Special Refractory Materials" with refractoriness greater than Seger Cone 32 (see p. 810).

[2] *La Céramique*, 1922, **25**, 153–157.

3. Thirteen clays contained less than 20 per cent. of alumina; of these, seven softened above 1650° C. and six below.

The relationship is not very definite, but appears to show that clays containing a high percentage of alumina are the most refractory.

The most successful attempt to correlate the refractoriness of a clay with its composition is that of Ludwig, who assumed (on a somewhat weak foundation) that the fluxes in a clay are in the form of a solid solution with the clay as solvent. He arranged the composition of a clay in the form of a formula with alumina as unity, thus: $x\mathrm{RO.Al_2O_3}.y\mathrm{SiO_2}$, and by plotting x as ordinates and y as abscissæ, obtained a chart (fig. 23) in which the diagonal lines represent the limits of the Seger cones marked thereon, so that the softening point of a clay is represented in terms of these cones.

This chart, helpful as it is for the more refractory clays, is quite unreliable if the total RO bases exceed 6 per cent., and is in any case only useful for comparison. The reason for its failure in certain cases is that even the best fireclays are not homogeneous materials and the fluxes[1] are not distributed sufficiently uniformly to admit of their being treated as solid solutions, though the errors in the case of the highest grades of refractory clays are, naturally, small.

This chart also shows—what has been confirmed experimentally—that, other things being equal, the more aluminous the brick the more refractory will it be.

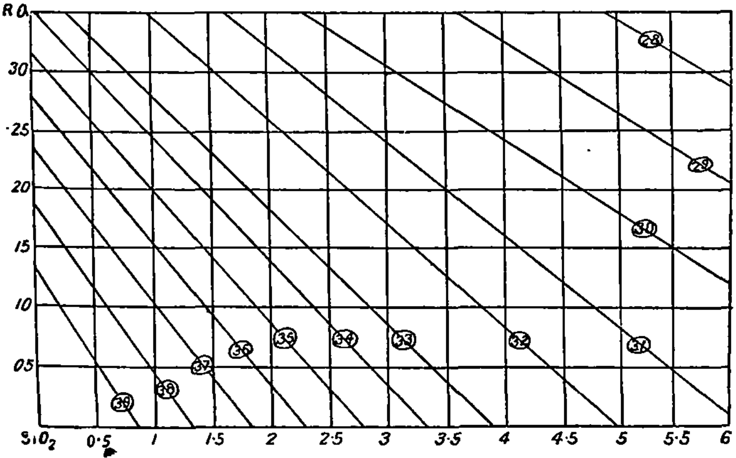

FIG. 23.—Ludwig's chart.

The addition of silica and of almost any metallic oxide (except alumina) will reduce the refractoriness of a fireclay, though if the added material is very coarse grained its influence will be less marked than if it is in the form of a fine powder.

Simonis found that in mixtures of kaolin, quartz, and felspar,[2] the latter acts as a constant and neutral flux, and in order to determine the softening point of such a mixture the percentages of kaolin, quartz, and felspar may

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[1] See footnote on p. 67.

[2] See Table II., p. 35.

be represented as k, s, and f, and if k is greater than $\frac{s}{3}$, the "refractory index" will be $R-\frac{s}{3}-f+60$. For bodies higher in silica, in which $\frac{s}{3}$ is greater than k, the "refractory index" is $\frac{2s}{3}-k-f+60$. The value of the "refractory index," in terms of cones, is given in the accompanying table.

TABLE XXX.—REFRACTORY INDICES AND SEGER CONES.

Refractory index . .	17·5	22·6	28	33·7	39·2	44·6	50	57·6
Seger cone . . .	14	15	16	17	18	19	20	26
Refractory index . .	65	72	80	89	102	114	127	141
Seger cone . . .	27	28	29	30	31	32	33	34

From these and other investigations it appears that the fluxing effects on the clay are in the following order, beginning with the highest—soda, potash, oxide of iron, lime, and magnesia. Weight for weight, soda fluxes more than potash. A mixture of potash and soda is more fluxing than either alkali separately. The alkaline silicates always give great fusibility to the compounds which they form with other silicates.

All clays will fuse completely at about 1100° C. when mixed with twice their weight of sodium carbonate or with a corresponding amount of calcium carbonate and ammonium chloride.

Ferr*ous* oxide produces a remarkably fusible silicate. The fusibility of double and multiple silicates depends on that of the component silicates. A silicate which is infusible *per se* may always be melted by combining it with a proper quantity of a fusible silicate, and many infusible or difficultly fusible silicates can combine with each other to form very fusible double silicates.

On account of the relatively low temperature at which they act, fluxes are always the most important constituents as regards the refractoriness of a clay. A high proportion of fluxes together with high silica is particularly risky, as this combination forms a very fusible mixture, though R. J. Montgomery and C. E. Fulton[1] have found that the maximum activity of the fluxes takes place when the ratio of silica : alumina is between 7·1 and 5·1.

Valuable as is the knowledge of the refractoriness *per se* of a clay, there are many considerations which must be borne in mind before the heat-resisting power of a clay under actual conditions of use can be ascertained, particularly when the clay is intended for use in the interior of furnaces (furnace linings), where, in addition to the direct action of the heat, the variations in internal pressure (owing to the expansion and contraction of the mineral by changes in temperature) produce strains which cause far more damage to the clay than the direct action of the heat itself. It is always difficult to ascertain, without actual trial, whether blocks or bricks made of a particular clay will efficiently resist the combined action of heat and pressure ; probably the best way is to build a few of the bricks into a furnace lining, to watch them, and to carefully note their behaviour in comparison with bricks of other clay in a similar part of the furnace. The resisting power of fireclay to the action of molten steel and other metals is generally ascertained in a similar manner ; experiments on a very small scale are often unreliable.

[1] *Trans. Amer. Cer. Soc.*, 1917, **19**, 303.

The sizes of the particles, and the porosity or the density of the material, as well as its actual composition,[1] are all important; and, according to the purposes for which it is required, articles made of a refractory clay must be burned to an open or porous mass, a mass with an open interior but a dense surface, or as dense a material as can be produced. No one material can possess all the multifarious characteristics demanded, and users of firebricks and other refractory goods must, therefore, decide which characteristics are of minor and which of major importance.

It should always be borne in mind that the behaviour of a clay depends upon other conditions besides its composition, so that two clays of almost identical analysis may differ considerably in their refractory quality.

Burned Fireclay has properties quite different from those of the raw clay, on account of the changes effected by heat. In the first place, the clay loses its odour, becomes much harder, and is rougher to the touch. It loses its power of becoming plastic when mixed with water, and is no longer ductile and malleable. In a few cases, it may retain its feebly magnetic power. Its electrical conductivity is decreased if the temperature has been sufficient to cause vitrification. Vogt, however, found that some porcelain crucibles have a sufficient conductivity to allow electrolysis and the removal of some potash.

The colour of the clay is also changed, the burned product being white, buff, red, brown, grey, blue, black, or mottled, according to the impurities present in the clay.

Clay which has been burned can no longer be broken up into grains of extreme minuteness by simple treatment with water; it does not slake and will not remain in suspension. Its original lines of cleavage have disappeared, and if the preparation of the clay previous to heating has been suitable, all traces of its original laminated, granular, or shaly structure have gone.

The strength of the burned clay will usually depend on the size of the refractory particles and on the extent to which fusion has occurred. As vitrification proceeds, the pores in the mass are filled, so that the tension and crushing strength of the material, *when cold*, is roughly inversely proportional to the porosity.

The strength of partly vitrified clay, *when hot*, is the opposite to that just mentioned, being roughly proportional to the porosity of the material, and inversely to the amount of fused or viscous material present.

The weakness or strength of clays at a high temperature is important in furnace construction, and for this reason Bleininger has proposed that the crushing strength of all firebricks should be tested at a temperature of 1350° C.

Resistance to abrasion, *i.e.* to wear and tear, is an important characteristic of burned fireclays.

The micro-structure of burned clays affords a valuable indication of the changes which occur during the firing. The material may be examined in the form of (*a*) fragments broken or chipped off larger pieces, (*b*) polished and etched specimens obtained from a fractured portion, or (*c*) as a transparency or thin section.

The fragments—whether plain or polished and etched with a very dilute hydrofluoric acid—are examined by reflected light under a low magnifying power, a ⅛-inch objective being the strongest used for this purpose. The polished specimens are troublesome to prepare, and, except under special circumstances, do not produce results very different from those obtained by

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[1] Bleininger has stated that the metallic oxides (other than alumina) in a fireclay should not exceed 0·22 molecular equivalents, the molecule of Al_2O_3 being taken as unity.

examining an unpolished fragment. Lomax has shown that if the specimen is ground moderately smooth, but without polishing, and a sheet of clear glass is then brought into optical contact with its surface by means of Canada balsam, an effect is produced which is, in many cases, equivalent to polishing the surface, but involves much less trouble.

By reflected light the coarser and apparently amorphous portions of the clay will readily be observed, and a considerable amount of information as to their proportions, sizes, and nature may be obtained in this manner. These form the bulk of the material, the particles being cemented together by means of a glassy mass, so that their edges are not always easy to distinguish, particularly in vitrified clays. Sometimes this cementing material may be removed by solution in very dilute hydrofluoric acid, but in many cases the other constituents are also affected by the acid.

The difficulty of recognising the various minerals present being so great when the specimen is too thick to be transparent, their identification is chiefly accomplished by the study of specially prepared sections, which are sufficiently thin to be studied as transparent microscopic objects.

Such sections should be mounted on a glass slip, and examined (*a*) as transparencies, and (*b*) by means of polarised light. In the former case, the transparency or opacity and the shape and colour of the materials present will be seen, but owing to the large proportion of semi-transparent fused material some of the crystalline matter will be unobserved. By means of polarised light, however, all the amorphous material is rendered opaque and almost invisible, as light after polarisation by passing between crossed nicols can only travel freely through substances in a crystalline form.

A method for determining the refractive index is described on p. 157.

The identification of crystals present requires a special training, though the lath-like crystals of sillimanite, formed on prolonged or repeated heating at 1200° C. or above, are easily recognisable, as they are practically insoluble in dilute hydrofluoric acid.

Burned clay has no binding power, in the sense in which this term is used in clayworking, nor has it any appreciable elasticity or extensibility.

Clay which has been properly burned should not shrink appreciably in use. If it does so, it is an indication that the material should have been burned at a higher temperature. This constancy of volume is very important in many refractory articles, and in the bricks used for furnaces, kilns, etc.

The behaviour of burned clay when treated with water is entirely different from that of the same clay when raw. It so closely resembles that of a mixture of silica and alumina which has been similarly heated that it is often assumed that heating to redness destroys the clay molecules, and that the character of the products depends almost entirely on the " impurities " present in the clay.

The porosity is increased if the temperature has not been sufficiently high to cause vitrification. The ability to produce a viscous slip is no longer present, though the burned clay may itself form a viscous fluid if heated to a sufficiently high temperature.

The behaviour of the clay towards acid and alkaline solutions is entirely changed. The action of these on burned clay is seldom appreciable unless the solutions are very strong or the clay insufficiently burned.

On exposure to the weather, burned clay is not appreciably affected, good bricks being among the most durable building materials. Little or no oxidation or reduction occurs in its constituents, and if suitable fireclay is used it can withstand the highest temperatures available, except, perhaps, those of the electric furnace.

Sometimes a **scum** forms on heating clay. This is due to the condensation on it of acid vapours, derived from the sulphur in the fuel and carried in the burning gases, which attack any lime in the clay and form a sulphate on the surface, or to soluble salts in the clay rising to the surface during the drying, and being converted into a white deposit on burning the clay in a kiln. This latter form of scum is sometimes known as **efflorescence,** and is a troublesome characteristic of some clays. It may often be avoided by adding barium carbonate to the raw clay, which will make any soluble sulphates insoluble. The scum due to condensation products on the clay can only be prevented by heating the clay with pure air (free from flue-gases) until it is at such a temperature that no condensation products can form.

A still more troublesome form of efflorescence is that which appears on the surface of the goods after they have been drawn from the kiln and stored for some time. Such efflorescence is due to external causes, such as piling the goods on a floor formed of ashes, concrete, or mortar, and leaving them exposed to the weather, or in some condition where the floor can absorb moisture. This moisture may be gradually absorbed by the goods, and with it the soluble salts it derives from the mortar, ashes, or concrete. When this moisture reaches the surface it evaporates, leaving the scum-forming salts on the surface of the goods. Such efflorescence can only be prevented by keeping the burned goods out of contact with ashes, mortar, or concrete, unless they can be kept perfectly dry.

When burned clay is heated in commercial furnaces it is subjected to a variety of conditions which may prove detrimental to it. Of these, the action of heat is usually of minor importance, that of slags and other materials in the furnace being much more serious; these are dealt with in greater detail in subsequent chapters, as so much depends upon the manner in which the clay has been treated and the shape of the articles made from it.

The effect of the *fuel* used in heating furnaces, etc., in which refractory clays are used is often overlooked. Thus, sulphur and water in a fuel are both highly detrimental, as explained on p. 97 and in Chapter XIV.

FLINT CLAYS.

Peculiarly hard, flint-like fireclays are found in several parts of the United States, particularly in Carboniferous deposits of Pennsylvania, Ohio, Maryland, Kentucky, and West Virginia, where they occur often underlying coal seams, and in the same bed with the plastic clay, the two showing no regularity of arrangement, and often differing but little if at all in chemical composition. They occur also in the Cretaceous deposits of Colorado and Georgia, and the Tertiary beds of Alabama, and are known as flint clays. Ordinary fireclays are plastic when treated with water, but flint clays retain their intense stony (flint-like) hardness, their conchoidal fracture, and their general structure, which is not unlike that of flint. They appear to have been formed by the gradual accretion of sedimentary matter of a clayey, as distinct from a more purely siliceous, nature, around a fossilised sponge or similar centre, or by the recrystallisation of colloidal sediments.

Flint clays are not plastic, though they may become so after much grinding and mixing with water. They are not used alone for manufacturing goods, but when fairly pure are added to excessively plastic clays to reduce the plasticity of the latter, though they are costly to grind. Many flint clays are impure and of very little value.

True flint clays do not occur in Great Britain, but the term " flint clay " is sometimes applied here to ordinary rock clays of unusual hardness; this use of the term should be avoided, as it leads to confusion with the true flint clays.

GROG.

Grog is burned clay which is added to the refractory clays used for making firebricks, grog bricks, glass pots, retorts, etc. The effect of adding grog to such clays is as follows:—

1. The amount of water required to make a plastic paste is less than with raw clay.
2. The shrinkage of the grog and clay mixture is less than that of clay alone.
3. The strength of the unburned material is decreased.
4. There is less tendency to overfiring.
5. The strength of the fired material is increased.
6. The apparent specific gravity is increased.
7. The apparent porosity is increased.
8. By burning the clay and then crushing the grog, a material with grains ot any convenient size may be obtained.

In the manufacture of refractory goods, grog is an important ingredient, as it enables them to withstand sudden changes in temperature, and has an advantage over sand and other forms of silica in that it does not swell when heated. The amount of grog required in a clay mixture varies for different purposes. For fireclay bricks and other small fireclay articles, 7 to 20 per cent. of grog is usually employed, but for chamotte or grog bricks and some larger articles, 30 to 80 per cent. may be employed.

The use of crushed firebricks as grog can only be advisable when the composition of the bricks is known and when they are quite new. The use of old bricks—with their adherent or absorbed slag—is never satisfactory, and, unless great care is taken, there is a great probability of undesirable materials being crushed along with the firebricks. The production of rough clots or bricks instead of heating the raw clay in a shaft-kiln is not objectionable, but the purchase of old firebricks from builders should be discouraged.

The use of a large quantity of grog in a clay mixture also reduces the proportion of alkalies present, as these are partially volatilised during the preparation of the grog. Hence, this forms a convenient method of slightly raising the heat-resisting power of a clay.

For successful use, it is important that the grog should be made from a suitable clay—the common practice of grinding up any old firebricks being by no means satisfactory—and some of the best qualities are made by burning a high-grade fireclay in a kiln out of contact with fuel, grinding the product to a coarse powder, and removing the dust by screens.

It is an excellent practice to set aside a certain proportion of the bricks in order to grind them up for grog. This is usually better, and not noticeably more costly, than burning the clay in a shaft-kiln. Rounded grog should be avoided, as they do not provide so satisfactory a grip as angular pieces.

The dust should be removed from grog if it is to be used for making refractory goods liable to be rapidly heated and cooled, but this dust may be employed for firebricks intended for resisting the cutting action of flames, corrosive slags, etc.

The grog should usually be of similar composition to the raw clay used.

On the Continent, a number of firms specialise in the production of a particular quality of grog which they sell as "chamotte." This is made by carefully heating the best selected fireclay to a temperature so high as to destroy all shrinkage (usually about 1400° C.), the lumps of burned material being then examined and any seriously discoloured portions thrown away.

Equally good or even superior material may be made by most owners of fireclay mines in Great Britain should the demand justify the erection of the necessary kilns, the existing ones here not being the best for the purpose.

Hitherto, the value of carefully selected grog as the chief constituent of refractory articles has not been fully appreciated in Great Britain, partly on account of the abundance of fireclays of specially good quality. As these become exhausted, the improvement in quality which may be effected by burning the greater part of the clay before use, and binding the particles of grog with a highly plastic ball clay, will become increasingly necessary.

The limiting amount of grog which can be employed is determined by the binding power of the clay; if too much is used, clay becomes unworkable, because of the diminished plasticity. If the binding power of the clay be raised by mixing it with solutions containing humic acids or tannin in the cas[illegible] clay paste, or baryta or soda in the case of clay slip, much more grog ca[illegible] from incorporated with the clay. British fireclays are not sufficiently binding [illegible] permit the addition of large quantities of grog to them. In other words, they are not such good binding clays as are the ball clays of Devon and Dorset. Consequently, in Great Britain it is customary to use only sufficient burned clay to prevent the natural clay from cracking, etc.; whereas abroad exactly the opposite method is employed, the burned fireclay (grog or chamotte) forming the chief constituent of the mass from which the goods are made.

Another reason why grog is so largely used on the Continent is the abundance of waste material, such as saggers, which can be bought cheaply from the porcelain works and ground up to make grog. It is better, however, to burn specially selected clay, and this is always done for the highest qualities of grog.

In order to prepare grog from raw clay, the lumps of clay may be picked out, placed in the kiln, and burned, or the material may be ground to powder, made into rough clots in a wire-cut brick machine, and burned in the kiln as bricks, or in shaft-kiln. The practice of grinding the clay before calcining is not desirable, as it tends to cause a large proportion of rounded particles. If it is possible, therefore, to either burn the lump clay or to make it into rough clots about 10 inches by 10 inches by 4 inches without undue grinding, this method is to be recommended, as a more angular grog is produced.

In burning clay for the production of grog, lumps of selected clay may be placed on top of the bricks, etc., in the kiln, and so are burned without any special attention. This method is convenient, but the grog is seldom of high quality, so that it is much better to prepare it in a kiln built and used for no other purpose. On the Continent, two types of kilns for chamotte or grog are employed—

(*a*) Down-draught kilns—preferably gas-fired—in which the lumps of clay are stacked in a similar manner to bricks. Such kilns may be arranged in series and worked as a continuous kiln. Kilns of this type cannot be used for clays which fall to pieces when burned; clay in lumps or bricks is essential.

(*b*) Shaft-kilns—preferably gas-fired—in which the raw clay enters at the top and the burned material is removed at the bottom. The most suitable kilns closely resemble the gas-fired ones used for burning lime. Shaft-kilns have the advantage of requiring no "setting," and small pieces of clay can be used along with the lumps. Hence, shaft-kilns are considerably cheaper to use. If heated by gas, they produce a perfectly clean grog, which on the Continent demands a ready sale at a profitable figure. As shaft-kilns for grog are continuous in action, they cannot be used for an output of less than 5 tons per day. The chief disadvantages of shaft-kilns for burning grog are—

1. Their liability to become choked, with the result that the grog is not burned uniformly. This can, to some extent, be avoided by blowing or drawing air through the material during the burning.

2. The heating is irregular unless the man in charge is both skilled and conscientious.

Rotary kilns have been used for burning grog, but are unsuitable, except where the output is very large. The cost of installing and maintaining a rotary kiln is considerable, and there is some uncertainty as to the uniformity of the heating.

The temperature reached in burning the grog is important; if soft-fired grog is used, the shrinkage of the bricks is very great; if the grog has been fired moderately hard (say, Cone 9), somewhat better bricks are produced; by far the best are those in which hard-burned grog (Cones 12 to 14) is used. short, the harder the material to be used for grog is fired, the better will the quality of the finished bricks. The great essential is that the grog should be burned at a higher temperature than any it is likely to reach when goods made from it are in use. It is not sufficient to use soft-fired grog and to burn the goods to a high temperature, as this does not give as satisfactory a material as that in which hard-fired grog is employed; this is partly due to the loss of alkalies and silica[1] and to other changes which occur on repeated heating. Grog fired at excessively high temperatures is said to be "dead," because the clay will not bind so much as if the grog has been fired at a lower temperature.

Free silica in the clay used for making grog is undesirable, as it expands on burning, and in doing so will strain and weaken the bond and reduce the breaking strain of the whole mass.

It need hardly be said that the material used for the manufacture of grog should be quite free from glaze, fluxes, or clinkered pieces of material. Very great care must be taken not to contaminate the grog with ashes from the fuel used in the kiln; this is one of the chief reasons for using gas-fired kilns.

The addition of comparatively coarse-grained, non-plastic material to a clay mass cannot increase its resistance to rupture under tension. All experiments go to show the contrary, just as occurs with concrete. The resistance to rupture of a mixture of clay and grog depends upon the compactness of the mass: in other words, upon the degree of closeness with which the constituents adhere. Any separation between grog and clay, or cracks in the particles of grog or the interstitial clay, at an angle to the direction of the tension, will lower the breaking strain, and it is just such planes of separation or shrinkage cracks which give destructive vapours and fluxes their chance to enter the mass.

The breaking strain serves to measure the degree of coherence of the mass, and in consequence supplies useful information as to the most suitable temperature of burning. When the breaking strain reaches a maximum, it is certain that the particles forming the mass are knit together as closely as

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[1] In 1897 E. Cramer discovered that when fireclay is heated in the presence of carbon or reducing gases, part of the silica is reduced to silicon, which then volatilises, some of the alkalies in the clay being volatilised at the same time. Hirsch found that volatilisation occurred on heating under oxidising conditions.

possible. The breaking strain also shows what is the best duration of burning. Some clays continue to gain in strength when kept a long time at the same temperature. This increases the amount of vitrification, and well-vitrified masses are usually exceedingly strong.

For use, grog must be crushed to a coarse powder and carefully graded into the desired sizes by means of sieves or air-separators. Stone-breakers, jaw-crushers, crushing rolls, disintegrators, and rotary mills are the machines chiefly used for this purpose. An edge-runner mill may, however, be used if desired. The particles of grog should be sharp and angular, and should be produced by "crushing" rather than by "grinding." An edge-runner mill with a perforated pan is excellent, though it produces more flour than is desirable. Crushing rolls are also good, but require the material to be supplied in pieces not more than 2 inches in diameter. Jaw-crushers do not give so large a proportion of dust, and have, therefore, an advantage in this respect. Disintegrators of the "cage" or "devil" type are very useful, but tend to introduce too much iron into the material. The best results have been obtained by breaking the material by hand or in a jaw-crusher until it passes through a hole 2 inches in diameter, then crushing it to pea-size between crushing set side by side, and finally in an edge-runner mill, the runners of which a arranged that they do not come into direct contact with the bed or pan of the mill, but leave sufficient space between to prevent the production of too much powder.

There is scope for a considerable amount of ingenuity in constructing a mill which will reduce firebricks or "lumps" of hard-burned fireclay to granules of suitable size, without, at the same time, producing more than a small percentage of powder, or unduly "rounding off" the edges of the particles.

A ball mill has the advantage that it creates no loose dust in the grinding house, but it makes the grains of grog rather too round, and usually produces too much fine flour. If worked in conjunction with an air-separator, a short ball mill is excellent for producing a grog, the particles of which are exactly of the shape and size required by makers of refractory goods.

When fine grog (grog flour) is required, a ball mill and air-separator form the best combination possible, and are greatly superior to an edge-runner mill.

The size of the grog particles is very important. When grog of various sizes is tested, it will be found that, the finer the grog—

1. The greater the proportion of water required to develop the plasticity.
2. The greater the shrinkage.
3. The greater the strength of the unfired body, if the grog is coarser than 200-mesh; with finer grog the strength is reduced.
4. The greater the shrinkage on burning.
5. The greater the strength of the fired body up to a temperature of 1450° C.
6. The greater the apparent porosity of the clay up to 1180° C. Between 1180° C. and 1300° C. there is little change in the porosity, and above 1430° C. the apparent porosity is decreased.

On the other hand, an increase in the size of the grog gives—

1. Greater porosity.
2. Greater resistance to sudden changes of temperature.

For most refractory purposes, a fine product is not required; on the contrary, all "dust" should be removed, as the smallest particles are less resistant to heat. Consequently, no particles of grog should be less than $\frac{1}{20}$ inch in diameter; the largest may be as large as peas ($\frac{1}{4}$ inch), and all intermediate sizes may be employed. A small proportion of grains as large as $\frac{1}{3}$ inch are not objectionable in large articles, but they must not be used in crucibles or in pots for melting glass. In some firms, it is customary to take all the grog that passes through a sieve of (say) ten holes per linear inch, but this is not really satisfactory, and a more careful grading of the grog will usually result in more durable articles.

Some brick manufacturers prefer to omit grog particles of certain sizes (*e.g.* all between 40-mesh and 60-mesh) and to use only coarse material and fine; others prefer to use all except the coarsest and finest particles.

No definite sizes can be stated as " best " for grog, as so much depends on the plasticity of the clay used and the nature of the goods to be made. It is usually necessary to make careful tests, using grog of different sizes in order that the best sizes for any particular articles may be found. W. E. S. Turner has found by experiments that the densest brick is produced when 50 per cent. of the material is smaller than the other 50 per cent., so that the smaller particles occupy the spaces between the larger ones; in this way, the proportion of voids is comparatively small and the brick is very dense.

F. A. Kirkpatrick has found that good firebricks may be made if the proportions of grog of various sizes are within the following limits :—

25–66·6 per cent.	20–40-mesh grog.
0–25 „	40–80 „
33–66 „	80-mesh dust grog.

These are only rough indications; the best method is to employ a mixture containing several sizes of particles, selected so as to produce a material in which the interstices between each successive size of grains are filled by smaller particles of grog, so that eventually there are practically no voids in the mixture. By this means a very dense mass is produced. The ordinary method of grinding produces too many particles of sizes which cause them to press against their fellows and separate them instead of merely filling the interstices between the larger sizes.

It is, therefore, better not to have a continuous gradation of sizes, but a selected series of sizes without some of the intermediate ones. For instance, a mixture might consist of 50 per cent. of non-plastic particles larger than 0·125 in., 35 per cent. of non-plastic particles between 0·025 in. and 0·010 in., and 15 per cent. of ball clay.

A useful rule is to make the volume of the larger grog particles double that of the plastic material and the fine grog particles, but it is essential that for every kind of article made from refractory material the proportions of the different sizes of materials which will give the best results should be studied. A good refractory paste may, in fact, be regarded as a kind of concrete in which the pebbles are represented by the coarse grains, and the cement (mortar) by the fine grains and clay. The material must be of this nature to obtain the best results, and, consequently, it is necessary to use carefully selected material. For articles which are required to withstand sudden changes of temperature, a larger proportion of coarse grog of uniform texture and little or none of the very fine grog is preferable, as such articles require to be somewhat porous. As a general rule it is better to have the grog too coarse rather than too fine; but if only large pieces of grog are employed, there is a tendency to lose strength owing to the reduced binding power.

One well-known firm divides its grog as follows: (*a*) grog remaining on a five-hole screen; (*b*) grog passing a five-hole, but remaining on a ten-hole screen; (*c*) grog passing a ten-hole, but remaining on a twenty-hole screen; (*d*) grog passing a twenty-hole screen. This firm only uses the (*b*) and (*c*) portions, returns the (*a*) portion to the mill to be reground, and accumulates the (*d*) portion for other purposes. Since separating in this way, the life of the saggers has been nearly doubled, owing to the greater exactness with which the proportions of materials of different sizes can be regulated.

In France, a somewhat finer grog is used than in this country, and separation is made into three sizes: (*a*) passing a five-hole sieve; (*b*) passing a ten-hole sieve; (*c*) passing a thirty-five-hole sieve. This last size (though popular) is too fine for other than very small saggers.

In Germany, "fine grog" is that composed of particles less than $\frac{1}{12}$ inch in diameter, and "coarse grog" that in which the particles measure between $\frac{1}{8}$ inch and $\frac{1}{4}$ inch. Pieces of grog more than $\frac{1}{4}$ inch in diameter are not used.

The individual grains of grog should neither shrink nor crack. Their shape should be such as to encourage close packing and interlocking, and the question of size needs consideration in connection with the work to which the bricks are to be put; yet it is not unusual to find firebricks with round grains of clay from $\frac{1}{4}$ inch to $\frac{1}{2}$ inch in diameter, cracked, and ready to fall out. Some clays, though shrinking very little, if at all, have a marked tendency to crack, and break up on heating into small, angular, and exceedingly from fragments, forming an excellent grog. When such clays are worked allel the mass in pieces larger than they would naturally break into on heating, they will split up inside the mass. No bond can possibly get into the cracks so formed, and such a grog becomes a source of weakness rather than strength.

Rounded grains have the further drawback of not packing well. Angular fragments pack much closer into one another, and for this reason are to be preferred. A tightly packed, non-shrinking, non-cracking grog tends to give a dense brick that is true in shape. The more permanent the skeleton the truer will be the body.

Fine grog gives a higher porosity than coarse grog, but the mixture is more sensitive to sudden changes, and at higher temperatures vitrification sets in more rapidly, thereby making a less porous and stronger ware than with coarse grog. A mixture of clay and fine grog stands a load well. Coarse grog is less sensitive to repeated heatings, but will not stand a load. The main disadvantage of using too large particles of grog is the brittleness produced in the goods, rendering them easily broken and very fragile.

The size of the grog has little or no effect on the contraction of the mixture as a whole, either for drying or burning at temperatures below Cone 15 (1435° C.), but in articles heated to Cone 20 (1530° C.) its influence may be important.

The grog should be stored under cover in a dry place, as it is spoiled by exposure to rain and damp. The effect of using wet grog in place of dry in firebricks, etc., has been shown by Wilson, Edwards, and Leese to reduce vitrification, as the finer particles of clay are carried by the water into the pores of the grog and so give the effect of a coarser texture than when dry grog is used.

Grog should always be soaked in water immediately before use as, if employed dry, much of the water in the moist clay enters the pores of the grog and produces too stiff a paste.

The refractoriness of a mixture of grog and clay will be proportional to the relative quantities and the refractoriness of each. The mechanical strength of such a mixture when burned will usually be less than that of the burned clay alone, but may be greater than that of the grog alone. If any fusible matter, such as felspar, is used as grog or is present in it, the strength of the burned mixture may be greater than that of either the grog or burned clay.

It is usual, when referring to a material as "grog," to imply that it is a burned fireclay, but the term "silica grog" is sometimes applied to ground silica rock used for the same purpose. This material is very useful for increasing the proportion of silica in clay mixtures which are deficient in that substance, but for general use it is not so satisfactory as clay grog or bauxite, for two reasons: (i) silica is liable to expand on heating and may cause trouble, and (ii) it may act as a flux and reduce the heat-resisting power of the clay.[1] Hence, its use should be avoided whenever possible, as, although cheap, it does not possess the qualities required in a grog to be used at high temperatures. For articles which are only exposed to moderate temperatures and where constancy of volume (*i.e.* neither expansion nor shrinkage) in use is essential, a mixture of fireclay and silica is extensively employed with satisfactory results. The use of grog which has previously been heated to above its softening-point has been patented (Eng. Pat. 217,897).

SILLIMANITE AND ALLIED MINERALS.

This group includes cyanite, andalusite, sillimanite, and mullite; it is of great scientific and technical interest because it includes the compounds formed when any mixture of alumina and silica is heated to any specified temperature. It then forms one or more of the following:—

(i) *Free silica*, which may exist in several forms, viz. quartz, tridymite, cristobalite, and vitreous (or fused) silica.

(ii) *Sillimanite*, $Al_2O_3.SiO_2$, which on further heating may form mullite.

(iii) *Mullite*, $3Al_2O_3.2SiO_2$, which on further heating may form corundum and free silica.

(iv) *Alumina*, which may be in the form in which it was present in the original mixture or in the form of corundum.

There is only one eutectic; it melts at 1545° C. and consists of 94·5 per cent. of silica and 4·5 per cent. of alumina.

If the melt is richer in silica than is mullite the mixture will consist of free silica and mullite, whereas melts richer in alumina than is mullite consist of corundum (free alumina) and mullite. The approximate decomposition temperatures are: cyanite 1325° C., andalusite 1350° C., sillimanite 1530° C., and mullite 1830° C. Hence, of the four minerals, *mullite* is the most stable. It is also formed when fireclay is heated to about 1000° C., though crystals of observable size are seldom formed below 1200°–1250° C. The other three minerals have the same composition, but they differ in crystalline form and other physical properties. When heated in the presence of soda or potash, the sillimanite group tends to form crystals of nephelite, $Na_2O.Al_2O_3.2SiO_2$, or leucite, $K_2O.Al_2O_3.2SiO_2$. These are readily identified by their low refractive index and weak birefringence.

At one time these minerals were confused with one another, and for some years the mullite in fireclay bricks was regarded as sillimanite. The confusion is easy to understand, as both in the shape of the small crystals and in chemical composition these minerals closely resemble each other. The existence of this important group of minerals is due to the fact that aluminium can form both tetrahedric (AlO_4) and hexahedric (AlO_6) groups. This explains the fact that whilst the simplest aluminium silicate, $Al_2O_3.SiO_2$, can crystallise in such

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[1] This statement does not apply to grog made of "fused silica."

different forms as andalusite, sillimanite, and cyanite (disthene), the grouping of the SiO_4-tetrahedra is different. In sillimanite there are four, in andalusite five, and in disthene six, oxygen atoms combined with the residual aluminium atoms.

Mullite ($3Al_2O_3.2SiO_2$) occurs rarely as a natural mineral, but is formed on heating sillimanite, cyanite, or andalusite either alone or in any proportions —and all mixtures of silica and alumina. It is present in burned fireclay bricks, in which it occurs as a felted mass of lath-like crystals. It may be manufactured commercially by adding sufficient alumina (usually bauxite), with a small proportion of flux to produce a mixture corresponding to the formula of mullite, and fusing this electrically or heating it in a blast-furnace to about 1200° C. (see p. 386). With perfectly pure alumina and silica, mullite is not formed below 1600° C.; with an accelerator (added purposely or as an impurity) the required temperature is 1350°–1380° C. The following accelerate the formation of mullite: alkali silicates, magnesia, iron oxide, felspar. A disadvantage of accelerators intended to increase the amount of mullite is the risk of the accelerator combining with any free silica present and forming a glassy matrix of very low refractoriness.

The form of mullite crystals often reveals their source. Those from cyanite grow largest on the outside of the mass and tend to lose their parallel arrangement. Mullite crystals from andalusite are all parallel in one direction, usually at right angles to the longest axis of the original crystals. Mullite crystals from sillimanite are usually small and lie parallel to the long axis of the original crystals. Mullite appears to crystallise in at least two (similar) forms,[1] but their separate properties have not been clearly distinguished. Moreover, W. Eitel[2] has shown that the formula for mullite is not exact, as some mullite crystals contain more alumina than is shown in the formula. X-ray analysis has also failed, so far, to indicate the structure of the crystal unit. These variations in the composition of mullite may also indicate an irregular space-lattice which is in process of change from sillimanite to corundum. Mullite prepared by calcining cyanite[3] at 1450° C. has the following properties: crystals rhombic, the dimensions of the unit cell being a=7·49Å., b=7·63Å., and c=5·74Å.;[4] specific gravity 3·0; apparent density 2·25; refractoriness about Seger Cone 36–37 (1815° C.). Mullite melts incongruently, *i.e.* it decomposes whilst melting and so has no sharp melting-point. The products of its decomposition are corundum (melting-point 2000° C.) and a complex glass which contains all the impurities.

The proportion of mullite in fireclay bricks or in the artificial product may be determined by treatment with hydrofluoric acid, which dissolves the other constituents but leaves the greater part of the mullite crystals unaffected. Mullite is highly resistant to alkalies, but is slowly attacked by molten glass.

Pure mullite melts at 1810° C., but it forms a eutectic with silica melting at 1545° C. Under ordinary conditions of heating, mullite bricks soften very little up to 1810° C. For this reason all well-burned bricks containing less than 72 per cent. of alumina have a lower refractoriness than those richer in alumina. On prolonged heating at 1550° C. mullite decomposes, forming corundum (Al_2O_3) and a liquid phase.

According to W. Hamilton Gordon[5] the coefficient of linear expansion

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[1] Partridge and Lait, *J. Soc. Glass Tech.*, 1936, **20**, 204.

[2] *Ber. deut. ker. Ges.*, 1937, **18**, 2–11.

[3] Through a misunderstanding some years ago this material was placed on the market under the name "sillimanite," and calcined cyanite is still sold under the name of "sillimanite."

[4] W. Büssem, *Ber. deut. ker. Ges.*, 1935, **16**, 381–392.

[5] *Refract. J.*, 1929, p. 291.

of mullite varies with the source of the material; the maximum expansion at 1765° C. (1·3 per cent.) was that of mullite made from andalusite; the expansion of mullite made by electrically fusing alumina and silica is 0·767 per cent. Mullite is a desirable refractory material as it shows very little softening below its melting-point (1810° C.) and is very insensitive to sudden changes in temperature, but it is not extensively used in bonded bricks because of the variations in the product and the high cost.

Edelmullite is made from South African sillimanite.

Sillimanite.—The happy discovery of large quantities of natural sillimanite in Northern India has led to the use of this substance as a refractory material, superior to fireclay, but much more costly. Natural sillimanite or fibrolite ($Al_2O_3.SiO_2$) has a melting-point of 1850° C., and usually occurs as long needle-shaped crystals and in fibrous aggregates. The crystals belong to the orthorhombic system, have a hardness of 6 to 7, and a specific gravity of 3·23. Pure sillimanite is colourless, but the natural mineral is often coloured brown by a small proportion of iron oxide. It is devoid of plasticity, and so must be mixed with clay before it can be moulded into any desired shape. It is exceptionally resistant to corrosion by fluxes, glass, etc., and is only with great difficulty attacked by hydrofluoric acid.

Owing to the great hardness of sillimanite, the ground material usually contains metallic iron. This can be separated by means of a magnet.

Pure sillimanite is stable below 1545° C., but at that temperature it dissociates slowly into mullite (p. 146) and a liquid. At 1700° C. the dissociation is rapid, and above 1800° C. sillimanite and mullite dissociate into corundum (Al_2O_3) and a liquid. With commercial minerals the decomposition occurs at rather lower temperatures than those mentioned. The expansion is slight and fairly uniform. The advantages claimed for sillimanite as a refractory material are:—

1. High softening-point, well over 1800° C.
2. Perfect stability up to its actual softening-point.
3. Very low coefficient of expansion ($0{\cdot}45 \times 10^{-5}$), which enables it to withstand sudden and severe temperature changes.
4. Freedom from volume changes.
5. Neutral reaction.
6. Great resistance to the corrosive action of many slags and abrasion of moving charges.
7. Equal efficiency in oxidising and reducing atmospheres.
8. Great strength, which is maintained up to its softening-point, so that it resists pressure, when hot, more than most refractory materials.
9. Very low electrical conductivity, cold and at a high temperature.
10. Moderately high thermal conductivity (10 B.T.U./hr./sq. ft./°F./in.).

Sillimanite is largely used in the manufacture of bricks, blocks, crucibles, saggars, refractory fittings for electrical appliances, tubes for surface combustion, pyrometer sheaths, etc. For these purposes it must be mixed with a refractory clay; in the mixture the sillimanite behaves as grog (see p. 140).

Sillimanite is easily mistaken for cyanite, and one well-known material is a cyanite which has been converted into sillimanite by calcination. The Assam material is a true sillimanite and needs no calcination.

Andalusite ($Al_2O_3.SiO_2$) is a colourless mineral (often stained grey to red by a small proportion of impurities) which crystallises in the orthorhombic system, the crystals being usually long prisms with a hardness of 7·5 and a specific gravity of 3·1 to 3·3. In the British Isles, the crystals are small and scattered, but large masses occur abroad. An important deposit of natural andalusite in the United States is used as the chief constituent of a refractory porcelain employed in the manufacture of sparking plugs, and is regarded as superior to artificially prepared sillimanite.

Andalusite is not affected by heating to 1325° C., but when heated to 1390° C.[1] it is converted into cyanite and sillimanite, and eventually into mullite and silica, with a smaller volume-change than occurs with raw cyanite. The chief commercial source of andalusite is in the Inyo range in eastern California. Andalusite has no appreciable shrinkage or expansion when heated to 1500° C. or below.

Dumortierite ($8Al_2O_3.6SiO_2.B_2O_3.H_2O$) very closely resembles mullite, but contains boric oxide. It is converted into mullite at 1250° C., the boron being volatilised. The chief commercial occurrence of dumortierite is in Humboldt, Queen Canyon, Nevada. Dumortierite has a very small expansion when heated and so can be used without previous calcination.

Disthene ($Al_2O_3.SiO_2$) is unstable above 1250° C. and is converted into mullite. It is often regarded as identical with cyanite.

The chief characteristics of the minerals in the sillimanite group (compiled from several sources) are shown in Table XXXI.

TABLE XXXI.—CHARACTERISTICS OF THE SILLIMANITE GROUP.

	Hardness.	Specific Gravity.	Refractive Indices.	Unit Cell, Å.	Volume Expansion, per cent.	Decomposition Temperature, ° C.
Andalusite .	7–7·5	3·1–3·2	1·632 1·638 1·643	*a* 7·76 *b* 7·85 *c* 5·56	5	1380–1400
Cyanite .	5–7	3·5–3·7[1]	1·712 1·720 1·728	*a* 7·09 *b* 7·72 *c* 5·56	16	1350–1380
Sillimanite .	6–7	3·0–3·3	1·659 1·660 1·610	*a* 7·43 *b* 7·85 *c* 5·74	6	1540–1550
Mullite .	..	3·16	1·640 .. 1·654	*a* 7·49 *b* 7·63 *c* 5·74	..	1810
Dumortierite	6–7	3·2–3·3	1·650	..	..	..

[1] At 1200° C. the specific gravity is 3·22, at 1500° C. 3·10, and at 1800° C. 2·97. Such changes show that conversion to mullite occurs before it can be detected by the microscope.

Cyanite (or **disthene**) ($Al_2O_3.SiO_2$) has properties very similar to those of sillimanite and andalusite, but is slightly softer. It occurs in northern India, Assam, Virginia, North Carolina, Wyoming, and British Columbia. The crystals of cyanite are triclinic, with four molecules in the unit cell, the dimensions of which are a=7·09Å., b=7·72Å., c=5·56Å., α=90° 5½′, β=101° 2′, and γ=105° 44¼′.[2] It is regarded as an ortho-silicate, as the SiO_4-groups are independent. Cyanite is not affected by heat up to 1000° C., but at 1100° C. it is slowly converted into mullite and silica; it is converted more rapidly

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[1] Some authorities give 1475° C., and others 1500°–1700° C.

[2] W. Büssem, *Ber. deut. ker. Ges.*, 1935, **16**, 381–392.

at a higher temperature. The decomposition is accompanied by a great increase in volume. Hence, before it can be used as a refractory material it must be heated to at least 1100° C. (preferably 1250° C.), when it is converted first into sillimanite and, later, into mullite.

The differences in the increase in volume are noteworthy and are probably due to andalusite and sillimanite being much less pure than cyanite. The great expansion of cyanite makes it essential that it should be calcined before use.

HIGHLY SILICEOUS MATERIALS.

Firebricks and other refractory articles are also made of highly siliceous materials, which are sometimes—though erroneously—termed siliceous fireclays. These materials contain from 75 to 99 per cent. of silica. Some of these materials correspond to silica which contains 10 per cent. or more of clay, together with a small amount of impurities. The most important of these deposits are—

(1) The so-called fireclay deposits in the limestone hills of Derbyshire, North Wales, North Staffordshire, etc., and various other "pocket clays."

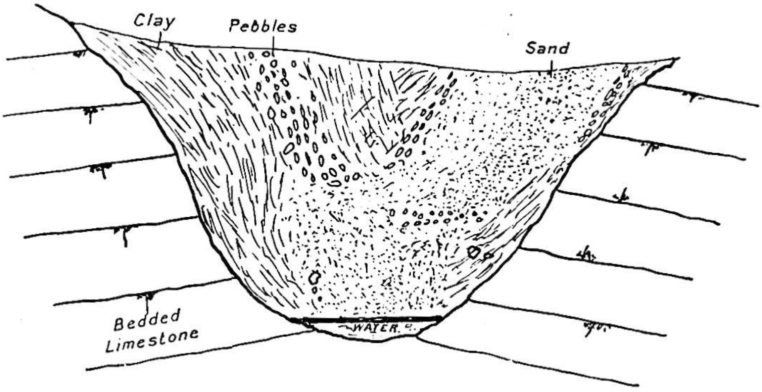

FIG. 24.—Typical sand and clay hole in mountain limestone. (Harris.)

(2) The more siliceous portions of the Coal Measure fireclays.
(3) Silica rocks, of which the Dinas rock may be regarded as the type.
(4) White sands containing at least 96 per cent. of silica.
(5) Quartzite pebbles found in limestone districts and in the Bunter beds.
(6) The ganisters of the Lower Coal Measures.

Pocket Fireclays.—These highly siliceous clays occur in the Mountain Limestone of Derbyshire, North Staffordshire, and more rarely in North Wales, and Ireland;[1] they consist of a mixture of fine white clay (coloured in parts) and clean sharp sand, often sharply separated, together with small amounts of other minerals derived from the limestone and the overlying Millstone Grit. Fig. 24 shows a typical cross-section of one of these pockets or "swallow-holes," many of which are very large and of considerable depth.

This clay has probably been carried to its present position by streams of water acting on the shales, sandstones, and grits on the higher ground. The bulk of this deposit in Derbyshire can only have been derived from Carboniferous Limestone rocks, the calcareous portion of which has been removed by solution; the clays and sands left have since become mixed with *débris*

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[1] At the present time the pocket fireclays in Ireland are entirely unworked.

from the overlying Millstone Grit. The presence of the quartzite pebbles (Bunter beds) can best be explained by assuming an extension of the Trias beyond Ashbourne, or that they were brought by glacial action.

The pocket clays are worked at Parsley Hay, Fridon, Alsop Moor, Brassington, Carsington, Minnington, Longcliffe, and Low Moor in Derbyshire, and odd pits are found irregularly scattered over other parts of Derbyshire. Unfortunately, they are somewhat difficult of access in spite of the railway. Other pockets occur on the north-western end of the Weaver Hills, near Oakamoor, in Staffordshire, and near Conway, Holywell, Bwlchgwyn, Llandudno, and Abergele, in North Wales. Those near Llandudno are, at present, not being worked. Unfortunately, the clay is often very impure and extremely variable in composition, though usually very plastic, and when fairly free from iron it is often valuable for architectural work and for sanitary ware. The average proportion of alumina in a large number of samples of this kind of clay is 10 to 14 per cent., corresponding to 25 to 35 per cent. of clay in the material, but occasionally richer clays are found.

The beds near Brassington are practically free from lime and magnesia, and are sufficiently low in alkalies and iron compounds to enable them to be used in the manufacture of good firebricks. Their comparative freedom from lime is very striking when it is considered that they occur as pockets in limestone.

The pocket fireclays vary greatly in colour, some being white, others yellow, red, purple, mottled, and even black. In most cases, these clays are very plastic when wetted. The sand which occurs in the same pockets is also very variable, ranging from the very finest grades to particles $\frac{1}{8}$ inch diameter. Most of the sand grains are rounded, though some angular ones may be seen; they are extremely white, and are mixed with abundant flakes of mica, which probably account for their brilliancy.

The whiter clays and sands are usually blended, and the material is chiefly sent to Staffordshire to be made up, though firebricks are made in considerable quantities in some districts where these clays occur—particularly near Wirksworth and Brassington in Derbyshire, and near Mold (North Wales). The materials should be carefully sorted before use, as some of them are not merely useless, but harmful.

SILICA ROCKS.

Silica rocks are very numerous, but in technology the term is restricted to those naturally occurring masses of silica which are suitable for use as refractory materials.

The chemical constitution of silica is discussed on p. 154. The generally accepted view that it may be represented by the simple formula SiO_2 does not explain many of the known properties of the various forms of silica, including the changes undergone by quartz which is heated and then cooled.

Such properties can be understood more readily in a substance of highly complex character and with a constitution corresponding to Si_xO_{2x}, the factor x being variable with the temperature and pressure. The behaviour of silica may be explained if a high molecular weight is accepted, but not otherwise.

Silica occurs in a number of different allotropic forms, some being amorphous and others definitely crystalline. The various forms are shown in Table XXXII.

The α-forms are stable at ordinary temperatures; the β-forms can only exist at, or near, the temperature at which they are formed. At any given temperature an equilibrium of both α- and β-forms of each variety of silica is usually produced.

TABLE XXXII.—ALLOTROPIC FORMS OF SILICA.

	Stable at	Specific Gravity.	Crystalline Form.
Crystalline.			
α-Quartz . . .	below 573° C.	2·64	hexagonal, trapezohedral, hemihedral.
β-Quartz . . .	573°–870° C.	2·65	hexagonal, trapezohedral, tetartohedral.
α-Cristobalite . .	1470°–1713° C. (unstable at 180°–1470° C., and especially 180°–270° C.)	2·22	regular.
β-Cristobalite . .	below 270° C. (unstable)	2·32	rhombic pseudoregular.
α-Tridymite . .	870°–1470° C.[1]	2·25	hexagonal.
β-Tridymite . .	117°–163° C.	2·27	(as α-quartz).
γ-Tridymite . .	below 117° C. (unstable)	2·27	pseudohexagonal rhombic.
Amorphous.			
Vitreous silica (fused quartz) . . .	below 1713° C.	2·20	..
Flint, chalcedony, etc.	..	2·56	..
Precipitated silica .	..	..	..
Cellular.			
Cellular silica (diatomite, etc.) . .	..	..	..

[1] Stable below 870° C. under some conditions.

The *melting-points* of the various forms of silica are:—

α-quartz—not known because it inverts without melting;
β-quartz—about 1470° C., but very difficult to determine on account of inversion;
cristobalite—1625°–1713° C.;[1]
tridymite—1670° C.;
vitreous silica—1713° C.;
cellular silica—1400°–1550° C.

Amorphous silica occurs in nature principally in the precipitated form as chalk flint, banded flint, opal, and hydrated silica (geyserite).

Flint occurs usually as irregular nodules or lumps of a grey to black colour, often covered with a white or yellow film. They are found principally in the Upper Chalk formation, chiefly in the counties south of the Thames, Suffolk, and in parts of Yorkshire; gravelly flints are found in Devon and Norfolk as well as in the south-eastern counties. Flints are supposed to be formed by the slow precipitation of silica around a nucleus consisting of a minute shell-fish, sponge, or other organism. They usually contain about 95 per cent. of silica, the chief impurities being organic matter and chalk, the former being

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[1] The melting-point of cristobalite appears to be above 1700° C., but owing to a wide vitrification range it is very difficult to determine it; 1713° C. is now generally accepted.

the cause of their dark colour. They break with a conchoidal fracture, and are of great hardness.

According to Roscoe and Schorlemmer, flint is an intimate mixture of amorphous silica and quartz or tridymite, but E. W. Washburn and L. Navias [1] favour the idea that flint consists of colloidal quartz.

When heated, flint may be converted into cristobalite, the crystals being larger than those formed on heating chalcedony, on account of the fluxes present in the flint.

Raw flint has an index of refraction, according to Washburn and Navias,[1] of 1·533 to 1·539; that of calcined flint is 1·483.

Chert or hornstone is an impure variety of flint produced by the deposition of siliceous sponges. It has a flat rather than a conchoidal fracture, and though really amorphous, it sometimes appears crystalline. It is usually grey, brown, or black in colour, and occurs chiefly in limestone rocks, particularly those of Carboniferous age. In this country, it is found in Derbyshire, Yorkshire, Durham, Northumberland, and also at Holywell, Prestatyn, and Ffrith in North Wales. *Lydian stone* is a variety of chert having a schistose structure of a very close grain.

Chalcedony is an opaque fibrous form of amorphous silica occurring in concretionary masses and in rock cavities, particularly basalts, and in flint nodules. According to Roscoe and Schorlemmer, chalcedony and agate are intimate mixtures of amorphous silica and quartz, or tridymite, though E. W. Washburn and L. Navias [1] consider it to be colloidal quartz, which, in the purest forms, is in the gel state, the particles being microscopical or sub-microscopical in size. It frequently surrounds a nucleus of some fossil or other fragment of foreign matter. It has a hardness of 7 and a specific gravity of 2·55 to 2·58. Its refractive index, according to Washburn and Navias,[1] is 1·533 to 1·538 in the raw state, which is rather lower than that of quartz; after calcination it is reduced to 1·456 to 1·47. The birefringence is also low. It is of a white, grey, pale blue, bluish-white, or brownish colour. On heating, it loses water at 100° C. to 200° C., the loss sometimes splitting the mass. It is characterised by a sudden expansion at 600° C.—probably a transition stage between hydrated silica and quartz. It becomes whitish and opaque, and gradually expands at 1000° C. to the extent of 0·5 to 4·0 per cent. Successive heatings do not cause further expansions up to the temperature to which it was previously heated, but the reversible change at 600° C. always occurs. On heating to 1400° C., the specific gravity is reduced to 2·3. *Buhrstone* is a variety of chalcedony of white, grey, or cream colour. Other varieties include *carnelian*, *prase*, *agate*, and *onyx*.

Opal is a form of hydrated silica—containing 5 to 10 per cent. of water—which may occur in compact, reniform, or stalactitic forms of various colours on account of its iridescence. It has a vitreous fracture and a low specific gravity (about 2·2), is softer than quartz (5·5 to 6·5 on Mohs' scale), is isotropic, and has a very low refractive index (1·45).

Siliceous sinter or *geyserite* is a loose porous form of amorphous silica formed by precipitation from the waters of hot springs, particularly in New Zealand, Iceland, and the United States. The geyserite found in Germany does not expand on heating to a temperature of 1410° C. This material is sold commercially for the manufacture of porcelain, earthenware, enamels, silica glass, etc. A material sold as geyserite, which occurs in the Taurus Mountains, is really a quartzite, and is crystalline, whilst true geyserite is amorphous.

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[1] *Journ. Amer. Cer. Soc.*, 1922, **5**, 565.

Hydrophane, hyalite, menilite, and *flint stone* are other forms of amorphous silica.

Silica glass occurs very rarely in nature; it has been named *Lechatelierite.* When prepared artificially, it is a valuable refractory material, and is known as quartz glass or fused silica (see Chapter XV.).

Colloidal silica occurs in different situations in nature, both in the form of a sol and as a gel. It may contain either a large proportion of water (up to 90 per cent.), or very small proportions when in the dehydrated gel state. It loses all its water at a red heat—the presence of salts rendering this loss more rapid—and amorphous silica is then produced, which can only, with difficulty, be reconverted into the colloidal state.

Colloidal silica gel is of considerable importance as a binding agent in natural quartzites. The gel does not form definite hydrates with water, but on drying loses water continuously, and at each temperature forms an equilibrium corresponding to the vapour tension at this temperature.

Crystalline silica occurs in nature, chiefly in the form of *quartz* (rock crystal, quartzite, sand, sandstone, etc.), but also as *tridymite* and *cristobalite,* though the two latter occur only rarely.

Quartz is a crystalline variety of silica occurring in hexagonal or rhombohedral forms, more or less developed according to its situation and mode of formation. It is found in massive, granular, or stalactitic formations. When pure, it is quite colourless, and resembles irregular fragments of glass, the edges being sometimes rounded by attrition. It is seldom found perfectly pure, but usually contains a small proportion of impurity, which may colour the crystals or cause them to become cloudy or even opaque. It has a vitreous lustre, conchoidal fracture, and a hardness of 7 according to Mohs' scale. Its specific gravity is about 2·65; its refractive index is 1·553 and its birefringence only 0·009.

There are three varieties of quartz:

(i) *α-quartz,* with long prisms having irregular pyramidal faces with transverse striations;
(ii) *β-quartz,* with short prisms having regular pyramidal faces and no striations;
(iii) *amorphous quartz,* known as *chalcedony, flint, chert, opal,* and *jasper.*

Each form of crystalline silica has a high- and low-temperature modification. The low-temperature (α-) form of quartz inverts into the high-temperature (β-) form at 575° C.

The crystalline structure of quartz consists of tetrahedral groups of oxygen atoms surrounding a central silicon atom. Each O-atom is shared between two Si-atoms, *i.e.* the tetrahedral groups are linked by having common corners. The quartz crystals belong to the trigonal system; they are hexagonal prisms with a hexagonal pyramid at each end.

In *α-quartz* the unit cell is hexagonal and contains $1+(4\times\frac{1}{4})+(2\times\frac{1}{2})=3$ atoms of Si and 6 atoms of O. The cell dimensions are $a=4{\cdot}901$, $c=5{\cdot}39$, $c/a=1{\cdot}10$, $u=0{\cdot}46$. The unit cell of α-quartz resembles that of β-quartz, but is slightly smaller, corresponding to a lesser molecular volume.

In *β-quartz* the unit cell contains the same number of atoms, but the dimensions are $a=5{\cdot}01$, $c=5{\cdot}47$, $c/a=1{\cdot}09$, $u=0{\cdot}50$.

Normally, quartz is the stable form of silica, but between 870° and 1470° C. it inverts into tridymite, and at a higher temperature or with the aid of a catalyst into cristobalite, which is the form of silica stable at the highest temperatures.

Although quartz is unquestionably a single chemical compound and should, therefore, have a sharply defined melting-point, in practice its melting-point cannot be expressed as a single figure, as so much depends on the size of the particles and the condition and rate of heating. The lowest temperature at which complete fusion has ever been known to occur is that recorded by Fenner, viz. 1470° C., but on a commercial scale, particles or masses of quartz only begin to show signs of softening at 1650° C., and do not appear to fuse below 1750° C. This wide range of temperature is largely due to the very low thermal conductivity of the material, whereby even a small crystal takes a large amount of heat to raise its temperature appreciably. In a direction parallel to its axis, the thermal conductivity of quartz is 0·028 calorie-grammes per second, whilst perpendicular to its axis, the thermal conductivity is only 0·016 calorie-grammes per second. The effect of the size of the particles on the thermal conductivity is shown by the following figures :—

Quartz	0·022
Silica bricks	0·003
Coarse sand	0·0009
Fine sand	0·00013

Quartz occurs in nature as—

(i) *Rock crystal*—the purest form—occurs in large flawless crystals, particularly in cavities in certain granites.

(ii) *Sands*, in which the particles of quartz are of varying sizes.

(iii) *Sandstone*, in which the particles of sand and other minerals are agglomerated by a siliceous cement.

(iv) *Quartzite*, which consists almost entirely of grains of quartz united with siliceous cement, the cement and quartz being more nearly homogeneous than in the case of less pure sandstones.

(v) *Firestone*, a porous silica rock which can be used in ovens and furnaces ; it is a form of sandstone which is distinguished by being more resistant to sudden changes of temperature.

(vi) *Quartz schist* or metamorphosed quartzite, generally resulting from mechanical deformation combined with obscure chemical changes due to the effect of heat.

(vii) Rarer forms, such as *amethyst*, *rose quartz*, *milky quartz*, *smoky quartz*, and *aventurine*.

Synthetic quartz is produced[1] artificially when large masses of glass are cooled slowly.

Tridymite[2] was discovered by G. von Rath[3] in trachyte and other volcanic rocks, in which it occurs in hexagonal plates, frequently forming triplets. Schuster and von Lasaulx have shown that tridymite crystals are pseudo-hexagonal, being formed by three separate orthorhombic portions which give rise to the appearance of triplets. It has never been found in large quantities, and is chiefly of interest as one of the products obtained by heating quartz to a high temperature.

Tridymite is seldom formed direct from quartz. On prolonged heating the quartz inverts completely to cristobalite, and only then do tridymite crystals form. By taking special precautions and using a mineraliser, tridymite can be formed direct, but unless the mineraliser is removed later the product may have a low refractoriness.

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[1] Wilson, *J. Soc. Glass Tech.*, 1918, **2**, 214.

[2] Tridymite is also termed asmanite.

[3] *Pogg. Annal.*, 1868, **133**, 507; **135**, 437.

A fibrous form of tridymite containing 7 per cent. of water found in nature is known as *lussatite.* Natural tridymite crystals are of the β-form, showing that this mineral has been formed at a higher temperature.

The transformation of the α- into the β-form of tridymite is rapid and reversible; it occurs, according to Mallard, at 130° C., and to Wright at 120° C., but Fenner claims to have found three forms, α, β, and β_2, the first inversion occurring at 117° C. and the second at 163° C. From these different results, it is obvious that the inversion-point is not sharp. β-tridymite forms uniaxial hexagonal crystals, the change in dimensions being less than when α-quartz is converted into β-quartz.

Tridymite has a specific gravity of 2·323 and a refractive index of 1·477; its melting-point, according to Ferguson and Merwin, is 1670° C.

Tridymite is the stable form of silica between 870° and 1470° C. It inverts very slowly to quartz below 870° C., and more rapidly to cristobalite above 1470° C. Tridymite differs from cristobalite in having a slightly lower refractive index (1·47), lath-shaped crystals, and wedge-shaped twins—with negative elongation and parallel extinction. Its inversion temperatures are also very characteristic. According to Eng. Pat. 220,603 tridymite is best made artificially by heating quartz, silica sand, millstone grit, etc., in the presence of a catalyst (such as phosphorus pentoxide, sodium tungstate, borates, sulphur trioxide, molybdic acid, phosgene, or sodium chloride) introduced into the atmosphere of the kiln, and heating under reducing conditions at first, but oxidising ones later.

Tridymite is preferable to cristobalite in silica bricks for various reasons, including: (i) it has the least thermal or temporary expansion of any form of silica; (ii) it has the greatest specific volume; (iii) it is less susceptible to sudden changes of temperature than any other form of silica; and (iv) it is the most stable form of silica at the temperatures at which silica bricks are used.

Cristobalite was also discovered by G. von Rath[1] in the same rocks in which tridymite was first found, and has also been found, according to A. F. Rogers, in minute spherical aggregates in spherulitic obsidian. It is a rare mineral, and is almost always associated with tridymite. Like the latter, it is chiefly of interest as one of the products obtained by heating quartz. It is best obtained by heating precipitated silica at 1400° C. for 48 hours.

Cristobalite crystals belong to the quadratic system, though triplets are common, and cause the crystals to appear to be pseudo-cubic. It has a specific gravity of 2·318 and a refractive index of 1·484. Its melting-point, according to Ferguson and Merwin, is 1710° ± 10° C. So many figures, however, have been published as the melting-point of cristobalite that it cannot be considered as definitely determined.

The specific gravity of cristobalite is always uncertain, as almost invisible cracks in the crystals and a metastable form cause low figures to be reported. There may be a continuous gradation from perfectly crystalline cristobalite ($d=2{\cdot}33$) to amorphous or vitreous silica ($d=2{\cdot}20$).

Cristobalite is the stable form of silica above 1470° C. Below 1470° C. it is unstable, but may persist in a metastable form for long periods. The high-temperature regular form (α-cristobalite) inverts with 28 per cent. increase of volume to a rhombic form (β-cristobalite) at temperatures from 275°–220° C. on cooling and at 198°–240° C. on heating. (The cause of the difference in the inversion-temperature is unknown.)

Cristobalite is recognised by its refractive index (1·48–1·50), optical sign,

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[1] *Pogg. Annal.*, 1868, **133**, 507; **135**, 437.

and the reversible change of state at 200°–275° C. with its large change in volume; this last is so much greater with cristobalite than with tridymite as to be quite characteristic. Multiple twinning in bands of one or two intersecting sets is common. Elongated units may show extinction at any angle.

According to M'Dowell,[1] when cristobalite is heated to a temperature of 230° C. to 275° C. it becomes isotropic, due to the formation of β-cristobalite. The reversion-point varies between 200° C. and 240° C. The formation of isotropic crystals cannot be used as a method of identification, because isotropicity may be produced in other ways apart from the transformation mentioned. Crystals of cristobalite are rarely seen in perfect form in silica bricks, the mass usually showing numerous circular cracks or crevices, giving the appearance of a number of tiny spheres. It has been suggested that the cracks are caused by rapidly passing the transformation-point at 230° C. to 275° C. in cooling, as at this point a contraction of 1 per cent. occurs.

The great change in volume which cristobalite undergoes at about 230° C. is the chief cause of the extreme sensitiveness of silica bricks at and near this temperature, and it is the more serious as the α-cristobalite breaks down into numerous separate crystals. The change is not confined to one of crystal-symmetry but to the formation of crystals of a different system. The inversion is accompanied by a characteristic change in colour, α-cristobalite being brown and β-cristobalite milky-white.

The identification of the various crystalline forms of silica is difficult, and requires the use of a special form of microscope and considerable manipulative skill. Cristobalite and tridymite are distinguished from each other and from quartz by means of their crystalline structure, refractive indices, and specific gravities, though the latter is only applicable to a limited extent. Thus, quartz is generally found in irregular grains, whilst tridymite forms perfect needle-shaped prisms, and when quartz is examined by polarised light, it shows a greater birefringence than either tridymite or cristobalite; but tridymite and cristobalite cannot be separated from each other in this way, as the difference is too small.

Quartz may also be distinguished from tridymite and cristobalite by immersing the powdered material in a liquid of specific gravity 2·40 (a mixture of bromoform and benzine being suitable), when the tridymite and cristobalite will remain suspended and the quartz will sink to the bottom of the liquid. Tridymite and cristobalite cannot be separated in this manner, as their specific gravities are too close together.

The most satisfactory method of distinguishing cristobalite, tridymite, and quartz from each other is by means of their refractive indices. In the method advocated by A. B. Dick, and largely used by the author, a little of the powdered material to be examined is immersed in an oil having a refractive index about the same as the sample, and the glass slip containing it is placed on the stage of a microscope and is illuminated by the use of a dark-ground illuminator, a yellow monochromatic light being used. Fringes will then be seen round the fragments of the sample, and if the liquid and the sample both have the same refractive index, the fringes will have a deep ultramarine tint, whilst if the liquid has a higher refractive index, the blue colour is paler and brighter or even white. If, however, the liquid has a lower refractive index than the sample, red or orange fringes are produced, these also becoming paler and brighter. Mercury-potassium iodide solution is a very satisfactory

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[1] *Trans. Amer. Inst. Min. Eng.*, 1916, 1, 999.

liquid for use in the test. For a yellow sodium light, this solution should have a refractive index of 1·477, which is the refractive index of tridymite, so that cristobalite—which has a refractive index of 1·484—can readily be distinguished in this liquid, the test being so sensitive that, if the solution is properly prepared, error is practically impossible. The refractive index of quartz is 1·553.

Cellular silica occurs in nature in the form of *kieselguhr* (otherwise called *diatomite*), tripoli, and randanite, and consists essentially of the siliceous skeletons of minute aquatic organisms. The various kinds of cellular silica are described on p. 180.

The Action of Chemical Agents on Siliceous Materials.—The chemical properties of silica depend chiefly on the fact that it is an acid whose action is most powerful at high temperatures. The resistance of siliceous materials to the action of chemical agents varies with the different forms of silica. Generally speaking, all forms of silica are insoluble in ordinary acids, but dissolve more or less rapidly in hydrofluoric acid in the cold, and in phosphoric acid at 400° C. or higher temperatures. Crystalline quartz is the least soluble in these acids and amorphous silica the most soluble.

Schwarz[1] treated various forms of silica with a 1 per cent. solution of hydrofluoric acid for one hour at a temperature of 100° C., and weighed the residue so as to find the amount dissolved. The following were the results obtained:—

Quartz	5·2	per cent.	dissolved.
Tridymite	20·3	„	„
Cristobalite	25·8	„	„
Gelatinous silica . . .	52·9	„	„

The action of *alkalies* upon siliceous materials is somewhat similar to that of hydrofluoric acid. Amorphous silica is more readily soluble in caustic soda than is quartz, and it is also soluble in sodium carbonate solution. W. Ostwald has sought to explain the difference in solubility of siliceous materials by suggesting that it is due to the different forms of silica being in various degrees of dispersion, ranging from the crystal (quartz) through chalcedony, hyalite, geyserite, and soft opal to a soft silica gel, the proportions of water varying progressively with the degree of dispersion. Thus, quartz having a low dispersion is less soluble, whilst colloidal silica or finely divided quartz is much more readily affected.

The action of *bases* upon silica is to form more or less fusible silicates, which when formed on a commercial scale are termed *slags*. If magnesia is present, the fused silicates tend to be viscous, but those rich in lime or alkalies are mobile.

With respect to the action of *lime* upon silica at high temperatures, Hedvall found the following results at 1000° C.:—

(*a*) Dehydrated precipitated silica reacts very rapidly with lime.
(*b*) Quartz glass reacts feebly at this temperature.
(*c*) Quartz and cristobalite do not combine with lime below 1400° C., the cristobalite being slightly more resistant than quartz.

Carbon attacks silica at all temperatures above 1200° C., forming silicon and carbon monoxide, and, in some cases, silicon carbide. The presence of iron and some other metals favours the reduction of the silica.

The Action of Heat on Siliceous Materials.—When amorphous silica is

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[1] *Z. anorg. chem.*, 1912, **76**, 422.

heated, it shows, according to Houldsworth and Cobb,[1] an endothermal reaction from 80° C. to 130° C., which is possibly due to the expulsion of water from the colloidal matter present; at 330° C. to 355° C., an exothermic reaction was observed, both these changes being irreversible. On heating strongly, it is converted, with some difficulty, into the crystalline form. Houldsworth and Cobb found that an amorphous silica, containing 5 per cent. of soda, was converted into cristobalite on prolonged heating at 700° C.

E. W. Washburn and L. Navias [2] consider that, on heating, chalcedony is partially converted into colloidal cristobalite, whilst the remainder forms isotropic silica glass, which very slowly crystallises into cristobalite. This may account for the range of refractive index exhibited by calcined chalcedony, and also for the absence of a definite α–β transition-point, this latter being possibly diffused over a long range of temperature.

Fenner,[3] however, found that, at 800° C., in the presence of a flux, chalcedony is converted into quartz and tridymite, the former disappearing on further heating.

The conversion of precipitated silica into quartz by heating it with water, under pressure, to 300° C. to 400° C., in the presence of a mineraliser, such as carbon dioxide, sodium carbonate, boron fluoride, or sodium silicate, has been effected by several investigators.

Similarly, by heating dry precipitated silica with sodium tungstate, alkali phosphate, lithium chloride or vanadate, or sodium molybdate, small crystals of quartz have been produced, though it is probable that cristobalite or tridymite were also formed. Without a mineraliser it is difficult to obtain crystals, but the recent work by Kyropoulos and Braesco respectively confirms the formation of cristobalite on heating precipitated silica to 1100° C. to 1300° C.

According to Fenner,[3] amorphous silica, in the absence of a flux, changes completely into cristobalite on heating to 1030° C. for 69 hours.

Crystalline quartz may be converted by the action of heat into some other allotropic form. According to H. le Chatelier and B. Bogitch, the change may be effected in three different ways—

(i) By the solution of the quartz in the melted silicates and its recrystallisation as tridymite at a temperature of about 1200° C., and by the melted silicates, on prolonged heating at or above 1500° C., dissolving some of the tridymite, which, on cooling rapidly, crystallises as cristobalite.

According to Groume Grjimailo, the tridymite and cristobalite are less soluble than the quartz, and so are rapidly thrown out of solution in the fused material when the latter is cooled slightly (see Table XXXIV., p. 163).

(ii) By the conversion of the fragments of silica under the influence of heat and in the presence of natural impurities, such as clay, etc., into some other allotropic form.

(iii) By the influence of foreign vapours which diffuse into the grains. Cristobalite is said to be very susceptible to such transformation, and Mellor and Emery have shown that flue-dust appears to aid in the conversion of silica into forms of lower specific gravity, even in parts of the bricks which are out of actual contact with the dust; the effect is probably due to the vapours from the dust.

When quartz is heated to a temperature of 575° C., it becomes β-quartz. This change, and a small one occurring between 200° C. and 275° C., are the chief causes of cracking and spalling on heating or cooling silica bricks too quickly at about these temperatures. The change is also accompanied by an

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[1] *Trans. Eng. Cer. Soc.*, 1922-23, **22** (ii), 111.

[2] *Loc. cit.*

[3] *Amer. J. Sci.*, 1913, **36**, 331-384.

endothermal reaction, which, according to White, is 4·3 calorie-grammes per gramme.

β-quartz crystallises in the hexagonal system, and the conversion from α- into β-quartz is accompanied by a sudden change in the properties of the material, including the effect of polarised light. The transformation is reversible, and, on cooling, β-quartz is converted into α-quartz, which, however, differs slightly from common quartz; a material similar to the former has been found by Wright and Larson in quartz veinstones.

When β-quartz is heated to a still higher temperature a second change occurs : the crystalline form is altered and *cristobalite* or *tridymite* is produced, though there is considerable uncertainty as to the precise conditions under which cristobalite and tridymite are formed.

According to A. Scott,[1] the principal details which affect the conversion of quartz into tridymite appear to be—

(1) The various non-siliceous materials present.
(2) The size of the quartz grains.
(3) The highest temperature at which the material is maintained.
(4) The time of " soaking," *i.e.* of heating at or near the maximum temperature.

It was at one time thought that the conversion could only take place at a very high temperature, but if the " soaking time " is sufficiently prolonged, the conversion may be completed at or near the temperature at which the conversion commences, the prolonged heating at a comparatively low temperature answering the same purpose as a much shorter heating at a higher temperature.

Ferguson and Merwin found that the minimum temperature necessary for the inversion of quartz into tridymite is 870° C., the rate of inversion increasing with the temperature, and being moderately rapid at 1300° C.

According to Endell and Rieke, it is impossible to fix a definite critical temperature on account of the slowness of the inversion at what appears to be the critical temperature ; inversion certainly occurs at, or possibly below, 1000° C., and is moderately rapid at higher temperatures.

Above 1470° C., tridymite tends to revert to cristobalite, so that in order to secure a large proportion of tridymite it is necessary to fire for a long period at some temperature below 1470° C. ; the conversion appears to be most rapid at 1410° C. to 1435° C. Le Chatelier found a continuous network of tridymite in well-fired silica bricks ; he attributes this network to the solution of quartz and its recrystallisation, first as cristobalite and then as tridymite.

The rate of conversion of quartz into tridymite is also increased by the presence of a molten liquid, such as fused felspar or calcium silicate, which has a solvent action on the quartz, or by the presence of a mineraliser, such as an alkali phosphate. The more viscous the liquid the slower the inversion, but as the temperature is raised and the liquid becomes more fluid, the inversion proceeds with a correspondingly greater velocity. For the same reason, molten calcium silicates, which are very mobile fluids, are so active that the quartz is converted directly into cristobalite, no tridymite being formed. Seaver found that under conditions of time and temperature which were required to invert 48·95 per cent. of a lime-free quartzite, no less than 77·35 per cent. would be converted if the quartzite contained a sufficient proportion of lime. According to A. Scott, the order of activity of various substances on the inversion-point of silica is as follows : iron oxide, lime, magnesia, titanic

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[1] *Trans. Eng. Cer. Soc.*, 1918–1919, **18** (ii), 481.

oxide, alumina; sodium and potassium silicates, chlorides and carbonates, sodium tungstate, sodium phosphate and lithium chloride also appear to facilitate the conversion of quartz into tridymite. The presence of more than one oxide usually increases the activity of the solvent, though this is not always the case.

The addition of sodium silicate (2 per cent.) containing 20 per cent. Na_2O, 62 per cent. SiO_2, and 18 per cent. H_2O, to quartz brings about a marked inversion below 1000° C. after at least an hour's heating. The rate soon diminishes, but the production of 95 per cent. cristobalite below 1050° C. is commercially practicable. A little cristobalite must be present to start the crystallisation.[1]

The formation of cristobalite is a subject of much controversy. According to C. N. Fenner, when ground quartz is heated to a temperature below 1470° C., only cristobalite is produced, and it has also been shown that amorphous silica, when heated in the absence of a flux, forms only cristobalite. On the other hand, some observers have shown that fluxes do not always interfere with its formation. Thus, Day and Lacroix have independently shown that when quartz is heated to about 1500° C. in the presence of fluxes, it forms cristobalite, and Endell has found that at temperatures above 1500° C., this inversion occurs even in the presence of lime, alumina, and iron oxides—substances which are supposed to favour the formation of tridymite.

Le Chatelier has found cristobalite in furnace linings composed of ganister and clay containing about 10 per cent. of metallic oxides, whilst it is invariably produced just below the metallic crust in Bessemer converters. On the other hand, he has shown that in many steel furnaces in which the temperatures are considerably above 1470° C., the bricks contained practically no cristobalite. This fact has been verified by several observers.

Bleininger and Ross found that at 1350° C., 57·13 per cent. of cristobalite was formed, and at 1450° C., 81·26 per cent. together with a little tridymite, whilst at 1500° C., 90 per cent. of cristobalite and a little tridymite were formed. Seaver found that at 1630° C., practically the whole of the mass had been converted into cristobalite with very little tridymite. By burning silica bricks at a temperature of 1450° C. for 40 hours, reburning some of these a second time and others a third time, under the same conditions, and separating the particles according to their refractive indices, he found that the products had the following average compositions :—

TABLE XXXIII.—EFFECT OF HEAT ON SILICA BRICKS.

	Quartz and Calcium Silicate.	Cristobalite.[2]
Silica bricks—		
After burning once	22·65	77·35
„ „ twice	17·13	82·87
„ „ thrice	16·02	85·98
Coarsely ground quartz rock—		
After burning once	50·57	48·95
„ „ twice	31·38	68·62

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[1] S. S. Cole, *J. Amer. Cer. Soc.*, 1935, **18**, 148.

[2] There appears to have been no tridymite in these samples (see above on the effect of a flux).

The much smaller amount of conversion of the pieces of quartz is due to the sizes of the particles having an important effect on the change of form, and tends to show that there are many factors which require to be considered in the formation of cristobalite. H. le Chatelier regards cristobalite as metastable at all temperatures below its fusion-point, and considers that it is only formed under special conditions, and that it reverts to tridymite whenever these conditions are not present.

The reversion of cristobalite to tridymite should, theoretically, occur between 1470° C. and 870° C., but Foxwell has suggested that it may change so slowly that it does not invert to any appreciable extent under ordinary conditions of cooling; this is contradicted by Fenner, who claims its unequivocal reversion between the temperatures stated above. He has shown that the presence of lime causes the inversion of cristobalite to tridymite, and, according to him, this action does not take place in the absence of a flux.

Each of the three crystalline forms of silica is converted, by the application of sufficient heat, into amorphous (fused) silica, which is the only stable form at the higher temperatures, and whilst, theoretically, quartz ought to be converted progressively into cristobalite or tridymite before fusing, it is possible, by heating it rapidly, to melt quartz before it has had time to be converted into either of its allotropic forms.

Some idea of the difficulties involved in determining the formation of the different forms of silica may be gained by remembering that if the quartz is powdered, the production of cristobalite is favoured; if crystals are heated, the low thermal conductivity interferes with the investigation. If the heating is rapid, the fusing-point may be passed; by heating slowly, the inversion may take place unawares.

Apparently, 1500° C. is the critical point at which quartz is converted into amorphous (fused) silica, 1670° C. that at which tridymite, and 1625° C. that at which cristobalite forms the same substance.

On cooling, the silica reverts back to its original form in the reverse order to that in which it was formed, if the conditions of cooling are suitable. Ordinarily, fused quartz does not crystallise, but retains its glassy form under all customary conditions of use.

If fused silica is maintained for a very long time above 1000° C., it is partially converted into cristobalite; the inversion is complete if the silica is maintained at 1500° C. for several hours. Le Chatelier has stated that cristobalite, being more or less unstable, tends to revert to tridymite if the action is continued sufficiently long. He states that any conditions tending to produce cristobalite will, if sufficiently prolonged, give rise to the formation of tridymite, *e.g.* in steel furnaces where the temperature exceeds 1400° C.

The crystallisation of fused silica with the formation of tridymite has been observed by Lacroix in some natural minerals, and by Le Chatelier in the case of a glass furnace, where the fused silica was maintained at about 800° C. for 20 days. It has also been observed by Day and Shepherd and Brun, but only in the presence of mineralisers; under these conditions, it is relatively easy to produce tridymite from quartz glass between 800° C. and 1500° C. This confirms Fenner's statement that silica is converted into tridymite between 800° C. and 1470° C.

The reversion of tridymite to quartz has also been observed by Mallard in natural minerals.

The conversion of fused silica into quartz by direct cooling alone has never been accomplished, but it has been effected by prolonged heating at 300° C. to 750° C. in the presence of a mineraliser; the temperature must not rise above

870° C. and not usually above 800° C. Thus, when silica, in any form, is heated sufficiently and then cooled, it will, *in time*, produce irregular crystals of quartz, the parts of which show various optical anomalies. The conversion of tridymite into quartz is, however, extremely slow.

C. N. Fenner represents the changes as shown in the following table:—

TABLE XXXIV.—CHANGES IN SILICA WHEN HEATED.

Temperature.	Product.
On heating to	
about 200° C.	α-quartz (hexagonal tetratohedric)
575° C.	β-quartz (hexagonal hemihedric)
870° C.	β-tridymite (hexagonal)
1470° C.	β-cristobalite (regular)
On cooling, the same products are formed in the reverse order down to 270° C., after which :—	
from 270–180° C.	β-cristobalite changes to α-cristobalite
120–115° C.	β-tridymite changes to α-tridymite and then very slowly into quartz

On a commercial scale, the various transformations mentioned above occur very slowly on account of the low thermal conductivity of silica, which plays an important part when dealing with large quantities.

The *volume changes* which occur on heating siliceous materials are very important, as upon them depends the stability, or otherwise, of articles made from them when subjected to sudden changes of temperature.

The volume changes are due to allotropic changes in the silica, which result in changes of specific gravity and consequently of volume. Below 100° C., quartz has a coefficient of expansion nearly twice as great perpendicular to the axis as parallel to it. The change from α- to β-quartz is accompanied by a change in volume of about 1·4 per cent., whilst at 870° C. there is an increase in volume of 14 to 16 per cent. If, however, the silica is in the form of chalcedony, the increase in volume (according to Washburn and Navias) from α-β is 2·6 per cent., that in flint is 3·0 per cent., that of cristobalite 2·8 per cent., and that of tridymite 0·14 per cent.

TABLE XXXV.—LINEAR EXPANSION IN VARIOUS FORMS OF SILICA.

Temperature, ° C.	Change.	Per cent.
117	γ-tridymite $\rightleftharpoons$ β-tridymite	0·27
163	β-tridymite $\rightleftharpoons$ α-tridymite	0·06
230	β-cristobalite $\rightleftharpoons$ α-cristobalite	1·05
573	β-quartz $\rightleftharpoons$ α-quartz	0·45
870	β-quartz $\longrightarrow$ α-cristobalite	6·60
	β-quartz $\longrightarrow$ β-cristobalite	4·85
	β-quartz $\longrightarrow$ α-tridymite	5·55
	β-quartz $\longrightarrow$ β-tridymite	5·50
1470	α-tridymite $\longrightarrow$ α-cristobalite	1·05
1700	α-tridymite $\longrightarrow$ quartz glass	1·05
	α-quartz $\longrightarrow$ quartz glass	17·5
	β-quartz $\longrightarrow$ quartz glass	20·0

The preceding table (compiled from data by various investigators, including Hodsman and Cobb [1]) shows the various changes in volume which occur during the various allotropic transformations of the different forms of silica.

The differences in the coefficients of expansion of the various forms of silica are also shown in fig. 25.

Table XXXVI, due to Rieke and Endell,[2] shows the changes in specific gravity of the chief forms of silica when heated repeatedly at about 1250° C.

TABLE XXXVI.—CHANGES IN SPECIFIC GRAVITY ON HEATING.

Material.	Specific Gravity.[3]											
	Raw.	Number of Times Heated in Oven.										
		1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Quartz from Norwegian pegmatite (in pieces)	2·65	2·38	2·33	2·325	2·33	2·32	2·31	2·32	2·33	..	..	..
Quartz from Norwegian pegmatite (in fine powder)	2·65	2·37	2·34	2·34	2·335	2·33	..	..	..	..	..	..
Quartz sand from Hohenbocke	2·651	2·591	2·502	2·456	2·450	2·442	2·428	2·386	2·369	2·343	2·338	2·328
Pure geyserite from Taurus	2·651	2·555	2·492	2·478	2·391	2·394	2·366	2·344	2·321	2·316	2·313	..
Average geyserite (ground)	2·651	2·456	2·361	2·349	2·333	2·317	2·306	2·307	..	..	..	..
Quartz crystal (St Gothard) (in pieces)	2·65	..	..	..	..	2·64	..	..	..	..	2·63	..
Quartz crystal (St Gothard) (in powder)	2·65	2·568	2·553	2·547	2·519	2·475	..	..	..	..	..	..
Flint (in pieces)	2·632	2·231	2·241	2·248	2·239	2·233	2·255	2·251	2·231	2·230	..	..
Chalcedony (in pieces)	2·607	2·16	2·17	2·17	2·19	..	..	..	..	..	..	..
Hydrated silica (Kahlbaum)	..	2·322	2·319	2·312	2·316	2·317	..	..	..	..	..	..
Quartz glass (Heræus)	2·21	2·327	2·328	2·33	..	..	..	..	..	..	..	..

For further information on the thermal expansion of various forms of silica, see Rigby and Green, *Trans. Cer. Soc.*, 1938, **37**, 364.

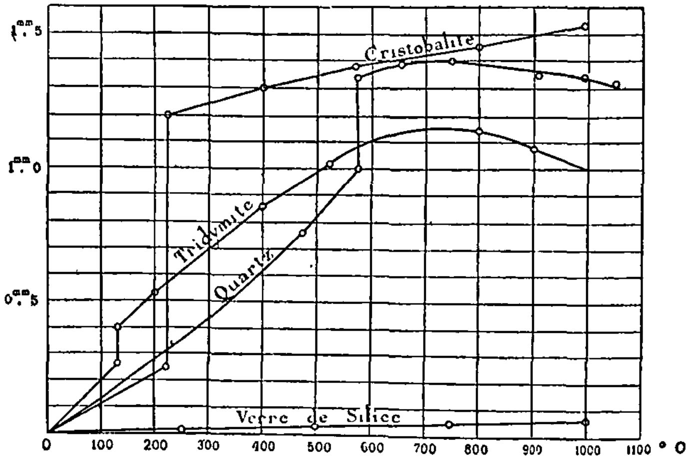

FIG. 25.—Percentage expansion of silica.[4]

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[1] *Trans. Eng. Cer. Soc.*, 1921–1922, **21** (iii), 227.

[2] *Silikat Zeitschrift*, 1913, No. 2.

[3] The specific gravity of quartz is 2.653, that of tridymite is 2.323, and that of cristobalite is 2.318.

[4] From data by Le Chatelier, and Holborn and Henning.

Quartz fragments expand greatly when heated, and are but little used for the manufacture of siliceous goods for refractory purposes. These are chiefly made of quartzite.

Although, as previously shown, silica is of very wide occurrence, only certain forms of silica are of value as refractory materials. These may be divided into four classes—

1. Silica rocks and quartzites which are more or less coarsely crystalline;
2. Sandstones and grits with medium-sized grains;
3. " Amorphous " quartzites having extremely fine grains; and
4. Ganister.

Other materials which have been used in the manufacture of silica bricks include—

Flints, which are useful, as their permanent expansion on heating is much more readily obtained than with other forms of silica. Clean flints containing about 98 per cent. of silica should be used. Flints which are contaminated with chalk are useless as refractory materials, but the flint pebbles found on the seacoast in the South of England and near Dieppe in France are much more pure, as prolonged grinding in the sea has removed almost the whole of the calcareous crust. Such flints are largely used as an almost pure form of silica. One advantage of flints is that, when heated to redness and then plunged into cold water, the silica cement is converted into a non-colloidal form of silica, and as the bonding agent is thus destroyed, the flints break up readily into very small fragments, which are reduced to powder much more easily than if the pebbles are ground without previous calcination.

Chert is seldom used as a refractory material, as it is, unfortunately, very difficult to grind, so that its use is limited to those occasions in which slabs or blocks of the natural stone can be employed.

Quartz schist has been used to a very limited extent.

Silica sand cemented by chalcedony has been used to a very small extent in America.

Khoetsky suggests that the most useful materials for silica bricks are as follows (in their order of merit): (i) chalcedony, (ii) old quartzites, (iii) vein quartz. He also states that quartz schist, sandstone, and sand are unsuitable materials on account of the large proportion of impurities usually present, and in the case of the last two because of the excessive fineness of the grains.

Quartzite is a rock consisting of an irregular mosaic of quartz crystals without any regular outlines, these quartz grains being united by a cement of almost pure silica which has been recrystallised or deposited in a colloidal state around the former crystal. In some cases, the outlines of the original grains can be readily distinguished, but in others this is very difficult. When the cementation has been sufficiently prolonged, the cemented grains fit so closely that they interfere and prevent the production of crystal faces; this has occurred in ganister.

The principal varieties of quartzite are: (i) *vein quartz*, which is produced as a result of hydrothermal action, and forms coarse interlocking crystals with little or no cement; (ii) *silica rocks*, which consist of grains of quartz cemented by siliceous material; (iii) *conglomeratic quartzite*, in which quartzite pebbles are cemented together by siliceous material; and (iv) *quartz schist*, which is a metamorphosed silica rock. When examined microscopically between crossed nicols, it shows bands and waves of colour due to distortion by pressure.

The principal quartzites in this country are found in Shropshire, Warwickshire, South Staffordshire, and Wales. They are chiefly of Ordovician, Cambrian, and pre-Cambrian age, though large deposits lying at the base of the Millstone Grit also occur in Wales.

The quartzite which occurs at Nill's Hill and Granham's Moor in Shropshire belongs to the Ordovician system and lies at the base of the Arenig series. It is of a greyish colour, the joints being stained yellow. The middle beds are true quartzite, whilst the lower part passes into a grit or sandstone. Felspar and mica, as well as some clay, occur in the interstitial cement.

In the Lickey Hills (South Staffordshire), a quartzite of Cambrian age crops out. It is a hard, grey rock, and in parts is stained a reddish colour. Kaolinite and sericitic mica are fairly abundant in the rock, and some chert also occurs.

The Hartshill quartzite of Warwickshire is of a pale pink or purple colour, and is inclined towards a sandstone. It is low in alkalies and iron oxide, but rather high in alumina. Felspar is fairly abundant in some parts.

In North Wales, useful quartzites occur near Bwlchgwyn, near Minera. These are of a white or pale grey colour, stained to some extent in parts, and containing some cherty material; felspar and mica are absent. A 6-foot bed of quartzite similar to that at Bwlchgwyn occurs at Trevor, near Ruabon, and is used for the manufacture of silica bricks.

In Brecknockshire, useful greyish, fine-grained quartzites containing some chert and felspar occur at Hirwaun and Penwyllt.

In Anglesey, pre-Cambrian and Ordovician quartzites occur; that at Porthwen is of a pale grey colour, containing a little sericitic matter but practically free from felspar. This rock is largely used for making silica bricks. At Holyhead, a massive, pale grey quartzite of probably pre-Cambrian age is used for silica bricks.

Some of the most important quartzites in Wales occur in Carmarthenshire and Glamorganshire, a quartzite at the base of the Millstone Grit series of Mynydd-y-gareg, near Kidwelly, being used extensively for silica bricks. Thick quartzites also occur at Bynea, near Llanelly, and near Llandybie. In Glamorganshire, the most important deposits are in the Vale of Neath, where the famous *Dinas rock* is obtained. This is a very pure stone, containing only about ½ per cent. each of lime and iron oxide and about 2 per cent. of alumina. It is a yellowish- or greyish-coloured rock having a pale bluish tinge; it is semi-transparent at the edges when carefully observed, and possesses many characteristics of crystalline silica or quartz. The Dinas material occurs both as rock and as sand with thin veins of clay, each form being of equal value and apparently consisting of the same material.

In Scotland, metamorphic quartzites occur in the Isle of Islay, and Jura, Argyllshire, and in Western Inverness-shire, round Loch Leven. Quartz schists occur round Loch Fyne, Argyllshire. The Scottish quartzites usually contain about 94·4 per cent. of silica; some contain also a small proportion of dolomite.

Owing to the many varieties of rocks from which quartzites may be derived, the chemical composition and physical characters vary considerably. In the proportions in which they usually occur in clays, these variations are unimportant, but where a highly siliceous material is used (as the so-called "clay" of Dinas, which is exclusively composed of quartzite and is almost free from pure clay) its origin is important.

Some of the purest quartzites are not of great value for silica brick manufacture, on account of their purity and the length of time required to convert the silica into a form in which it will not expand when the bricks are in use. There is an abundant supply of less pure, though more satisfactory, rocks, and until this is exhausted it is unwise to use a less suitable quartzose rock for making silica bricks. For making refractory bricks, a quartzite containing sufficient cement to unite the particles without reducing their fusing-point too seriously should be used, care being taken to employ a material in which the grains interlock to a considerable extent.

There are several varieties of quartzite which are not suitable for the best refractory goods, though largely used for bricks of good quality. The quartzites derived from geological formation earlier than the Coal Measures are seldom of much value for manufacturing purposes, though, as good and bad quartzites occur together, the geological formation is of little assistance to the brickmaker. For bricks, it is essential to use a true quartzite, *i.e.* one in which the particles of quartz are cemented together with a natural cement. When a quartzite is devoid of natural cement, the siliceous particles expand and have a marked effect on the masonry of which they form a part; the cementitious quartzites, on the contrary, expand so slightly as to be negligible, all the increase in volume of the quartz grains being counterbalanced by the elastic nature of the cement.

Wernicke has shown that any silica rocks of a wholly crystalline character (other than tridymite) are unsuitable for the best refractory bricks, unless a contractile bond, such as clay, is present or is added to them. His investigations have made it clear that the highest qualities of silica bricks can best be made from quartzites containing a suitable natural cement.[1]

The most suitable form of silica, and the one which, on the Continent, is being increasingly considered to be the only one from which the best silica bricks can be made, consists of quartzite pebbles—termed "*Findlings-quartzite*"[2]—which are freshwater deposits of Tertiary origin and belong to the period during which lignite was formed. They have been found in commercially useful quantities in limited areas in Germany, but they do not appear to occur in England or in the United States.

Under the microscope, the grains of quartz present are very small, with rounded edges, and are distributed uniformly through an amorphous ground mass of what Wernicke terms "basal cement."[3] Hence, the term "amorphous quartzites." Their origin is quite different from that of other quartzites, as they appear to have been formed of minute grains of sand, cemented together by a siliceous jelly, which gradually hardened and formed a siliceous cement. The accessory minerals in Findlings-quartzites are zircon and tourmaline. Rutile is never found, and muscovite (which is almost always present in other quartzites) is not found in Findlings-quartzite.

They expand almost to the maximum after a few hours' heating, and in this way are in marked contrast to other quartzites, and on repeated firings do not expand appreciably, hence, their great value as a refractory material.

The Findlings-quartzites have some resemblance to ganister, but the grains of the latter are larger. They have the advantage that, when crushed, the rock breaks into very minute crystals, so that the expense of fine grinding is rendered unnecessary. Findlings-quartzites are particularly useful for electric and other metallurgical furnaces where the requirements are very stringent. Figs. 26 and 27 (modified from F. Wernicke) show the structures of useful and useless quartzites.

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[1] M'Dowell has found, however, that the quartzites used for the best American bricks consist wholly of interlocking crystals, are free from cement, and so do not support Wernicke's statement.

[2] They are also termed *erratic block quartzites* and *amorphous quartzites*.

[3] This cement may be readily seen by soaking a thin section of the material in fuchsine solution, washing slightly and examining under the microscope. The cement will be stained by the dye, but the other particles will remain colourless.

Although the name "Findlings-quartzite" implies that this material is found in small, isolated masses, it also occurs in massive form, and the latter is the one chiefly used for brick manufacture.

Silica rocks resulting from the decomposition of felspar are useless for the best bricks, but some sands which consist of amorphous silica are quite satisfactory. These have a specific gravity of 2·33 to 2·45.

It will be seen that the chief characteristic of the rocks and sands most suitable for fire-bricks—those with a natural cement—is the rate at which they complete their expansion when heated. Endell and Rieke have shown that the amount of expansion depends partly on the surface area of the particles, but by selecting grains of uniform size they found that the cement quartzites reach the maximum volume and minimum specific gravity when heated for ten hours at 1300° C., and for five hours at 1400° C. to 1450° C., whereas other (unsuitable) quartzites required to be heated in this manner four or five times before this result was obtained. It is obvious that a form of silica which reaches its maximum volume in a single burning is preferable for brickmaking to one which continues to expand when in use. The change in volume is best determined indirectly by means of the specific gravity; Table XXXVII. by Endell and Rieke shows the specific gravity of five samples, before and after heating one to five times at 1450° C.

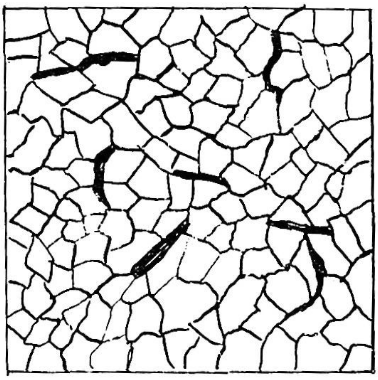

Fig. 26.—Useless quartzite.

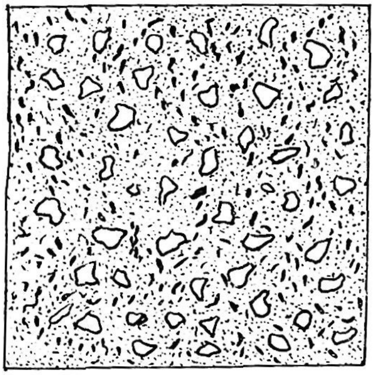

Fig. 27.—Useful quartzite.

(After Wernicke.)

TABLE XXXVII.—EFFECT OF REPEATED HEATING ON SILICA.

Sample.	Quality.	Number of Times Heated.					
		Nil.	1.	2.	3.	4	5.
A	good	2·65	2·40	2·40	2·38	2·32	2·38
B	good	2·65	2·40	2·37	2·37	2·38	2·37
C	medium	2·65	2·47	2·41	2·37	2·39	2·34
D	bad	2·64	2·51	2·50	2·47	2·38	2·34
F	bad	2·64	2·53	2·50	2·51	2·43	2·43

The following table shows the composition of the above-mentioned quartzites, and incidentally shows that chemical analysis and refractoriness alone are not sufficient for determining the value of a quartzite for making silica bricks:—

TABLE XXXVIII.—ANALYSES OF QUARTZITES.

	A.	B.	C.	D.	E.
Silica	97·85	98·36	98·82	96·04	99·04
Alumina	1·81	1·06	0·91	3·08	0·68
Ferric oxide	0·38	0·36	0·41	0·53	0·38
	100·04	99·78	100·14	99·65	100·10
Loss on ignition	0·32	0·22	0·18	0·46	0·08

All the samples had a softening point corresponding to Seger Cones 35 to 36.

The well-known Hohenbocke sand, which is particularly pure quartz, attained a specific gravity of 2·33 only after being heated eleven times; Dinas rock must be heated to 1500°–1600° C. for at least twenty hours to ensure the same result.

It is important to observe that in the best quartzites the impurities are in an extremely finely divided condition, whereas in less suitable silica rocks they are coarser and irregularly distributed.

For the best quality of silica bricks the quartzite used should have the following properties:—

(*a*) Under the microscope the quartz grains should be seen to be surrounded by a siliceous cement.[1]

(*b*) The impurities must be very finely divided.

(*c*) The maximum expansion and minimum specific gravity should be reached during the first burning to 1450° C.

(*d*) The material should contain 96 to 98 per cent. SiO_2.

(*e*) The softening-point must not be below 1730° C. (Cone 33).

These conditions are not generally known amongst British manufacturers of silica firebricks, and many thousands of pounds have been wasted in the past in useless endeavours to employ unsuitable varieties of silica rock.

Silica rocks in which the quartz grains show clear cracks should not be used, as bricks made from them tend to split along the cracks in the grains. Such cracked grains are most frequently found in the oldest rocks.

Sandstones are used to some extent for the manufacture of silica bricks. They consist of grains of siliceous material (furnished by rocks disintegrated by the weather, water, and other natural agencies) bonded together, more or less compactly, with some kind of cement, the type of cement frequently giving a special name to the sandstone as: siliceous sandstones, in which the bond is secondary silica, ferruginous, calcareous sandstones, etc. In some cases, sandstones are also designated by their predominant mineral constituents, such as micaceous and felspathic sandstones. Sandstones are generally more or less friable, and break with an uneven fracture. They are usually somewhat porous, and are liable to be stained by the intrusion of impurities in solution.

The principal impurities in sandstones are felspar and mica, but other

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[1] This is not absolutely essential if the grains of silica are sufficiently small and of such a nature that they are sufficiently converted into cristobalite or tridymite after once firing at about 1350° C. to 1400° C.

minerals may be present, such as chlorite, clayey matter, calcite, iron oxides, garnet, tourmaline, zircon, epidote, rutile, anatase, etc. Calcite is present as an impurity in some sandstones, such as in the Fontainebleau sandstone, Kentish Rag, Spilsby sandstone, etc., where it occurs in large crystalline masses.

The grey colour in sandstones is often due to fragments of shale, etc., or to the presence of ferrous carbonate or finely divided iron pyrites ; in exceptional cases it is due to iron phosphate.

Sandstones containing an excessive proportion of impurity are unsuitable for use as refractory materials.

Sandstones may be divided into several classes—

1. Coarse sandstones, as *grits*.
2. Loose sandstones, as *sand rocks*.
3. Impure brown or grey sandstones, as *greywackes*.

The sandstones which are most used industrially are the *grits* ; they are found mainly in the Millstone Grit formation. They are chiefly worked in the counties of Durham and South Yorkshire, and in Wales, though the Millstone Grit or "farewell rock" constitutes the lower bed of the Coal Measures as a whole. It also forms narrow areas immediately around the great coalfields of Wales, Yorkshire, Derbyshire, the West of England, and on the edge of Northumberland and Durham, though small areas of it are distributed irregularly some distance away. Thus, to the south of Hexham and Haltwhistle in Northumberland are several such isolated areas, whilst numerous others occur to the north-east of Sedburgh. A large Millstone Grit area extends from Lancaster to Settle and Garstang, and another large tract of it also occurs in West Devon, extending from Barnstaple to Tavistock and from Bampton to the Bristol Channel. The softer and purer portions are used in the manufacture of silica bricks, but, as previously explained, only those portions which have the necessary refractoriness and relatively small expansion can be used satisfactorily.

The commercially useful sandstones are usually less siliceous than some other materials used for silica bricks, the proportion of silica sometimes being as low as 80 per cent., whilst the alumina, alkalies, and combined water are invariably greater than in the purer silica rocks. Lime and magnesia, together with carbonaceous matter, are also sometimes in excess.

The Carboniferous sandstones consist of quartz crystals of medium size, some having sharply defined edges, but most of them being indefinite and separated from each other by a granular or amorphous ground mass. They are usually dark in colour, and sometimes contain carbonaceous matter as an "accessory mineral."

Some of these sandstones—known as "firestones"—are used where slabs of moderate, yet not great, refractoriness are required in furnaces, particularly in glass-manufacture and in the heat-treatment of steel.

Selected Carboniferous sandstones, when crushed and made into silica bricks, are largely used for steel works and coke ovens. When burned, they reach a minimum specific gravity more readily than the felsitic quartzose rocks but less rapidly than amorphous silica.

Ganister is a fine siliceous grit composed of minute, highly angular particles, forming a compact, bedded sedimentary rock of very fine granular texture. It sometimes contains a little clay.

The origin of the term "ganister" is unknown, but it was first applied, in connection with steel furnaces, to the fine dust carefully collected from the country roads between Sheffield and Penistone, which was rightly regarded as of great value on account of its refractoriness. As the demand for this material increased much faster than the supply, attempts were made to produce a similar material, by grinding the rocks used in making the roads. Laborious investigations eventually led to the recognition of certain outcrops of fine-grained silica rocks as being the most suitable for furnace linings, and the term ganister was, therefore, transferred to these rocks. Since then, the use of the term has been extended (unwisely in the author's opinion) to other silica rocks, some of which are quite unsuitable for furnaces, and this has led to much loss and disappointment. As originally the term "ganister" was applied to rocks of a certain geological horizon, viz. that immediately below the Ganister coal in South Yorkshire and Lancashire, it seems desirable to confine it to those rocks. The use of the term "ganister" for fine-grained silica rocks which lie just above the Millstone Grit in other coalfields is open to objection, as the properties of such ganisters are not identical with those of the "true ganister" of South Yorkshire. The still wider use of the term "ganister" to include siliceous rocks from other geological horizons should be abandoned as being incorrect and misleading, even though such rocks are used for some of the purposes for which true ganister is employed.

The term "true ganister"—when used in the following pages—is strictly confined to the fine-grained siliceous rocks which lie immediately below the Ganister coal; all other similar rocks are termed "bastard ganisters."

True ganister is extremely hard and difficult to crush, whilst other rocks which are sold as ganister may be reduced with comparative ease to the constituent grains of sand, of which they are almost wholly composed. The best ganister appears to be associated with an underlying fireclay.

Only a small part of the so-called ganister group of rocks is of value commercially, as the remainder is too impure to be used as a refractory material. The outcrops of ganister are specially sought, as they enable the material to be obtained more readily than from the deeper portions of the same beds.

The desirable features in ganister used for the manufacture of ganister- or silica-bricks are—

1. The angularity of the grains.
2. The evenness or uniformity of the grain-size. The best ganister rocks consist of grains 0·1 to 0·3 mm. diameter.
3. The interlocking of the mass.
4. The presence of only a small quantity of interstitial matter.

When the cementing material is almost wholly siliceous, the close interlocking of the grains is not so important.

Rocks with rounded grains are generally less pure, less compact, more friable, and more likely to receive infiltrated impurities.

The principal beds of ganister in Yorkshire and Derbyshire[1] are: (*a*) those forming the seat earth of the Soft Bed coal in Yorkshire or a small coal equivalent to it in Derbyshire; (*b*) the ganister under the Halifax Hard Mine, Ganister, or Alton coal (this being the *true* ganister); (*c*) the ganister under the "40 yards" coal seam.

What is regarded as the best ganister in England occurs between Ambergate and Penistone, the average thickness of the ganister group of rocks between Sheffield and Penistone being about 150 feet, but only about 6 feet is useful as a refractory material. The latter lies on a low-grade fireclay which, in its turn, lies on the Rough Rock forming the uppermost bed of the Millstone Grit. The order of the seams in this district is shown on p. 47 and in fig. 28.

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[1] The so-called ganister sands occurring with the pocket clays of Derbyshire are seldom satisfactory for the manufacture of ganister bricks, but if mixed with fireclay they make good semi-silica bricks (see Chapter III.).

At Deepcar, near Sheffield, the largest works obtains its ganister at a depth of 300 yards below the surface, but this is largely due to its having worked out the upper portions. In other parts of the same area the ganister is mined much nearer the surface. The ganister in this district varies from pale grey to buff, the predominant shade being a pale grey. It has an almost constant composition, averaging 97·7 per cent. of silica, about 0·35 per cent. of alumina, about 0·14 per cent. of potash, and about 0·28 per cent. of soda. There are practically no carbonates present, and a very low percentage of hydrated silicates. The great superiority of the Sheffield ganister depends on its physical properties rather than on its chemical composition. Its fracture is similar to that of chert; when ground, it breaks up into granular fragments, which interlock readily under slight pressure and can easily be made into very strong bricks. The grains are irregular in shape and are very small (0·002 to 0·006 inch diameter), but of various sizes, which interlock with each other and produce a very dense and hard material. True ganister contains a little clay, and some of the grains are usually united by a siliceous cement. Sericitic mica is abundant, particularly in the thicker parts of the beds, and iron stains are quite frequent, though irregularly distributed, some portions of the deposits being almost free from iron compounds. Felspar is rarely found, but does occur in some ganisters. Plant remains and carbonaceous streaks are very common, but as they burn out in the kiln and are never in sufficient quantity to do appreciable harm, the manufacturer does not usually need to feel concerned about them.

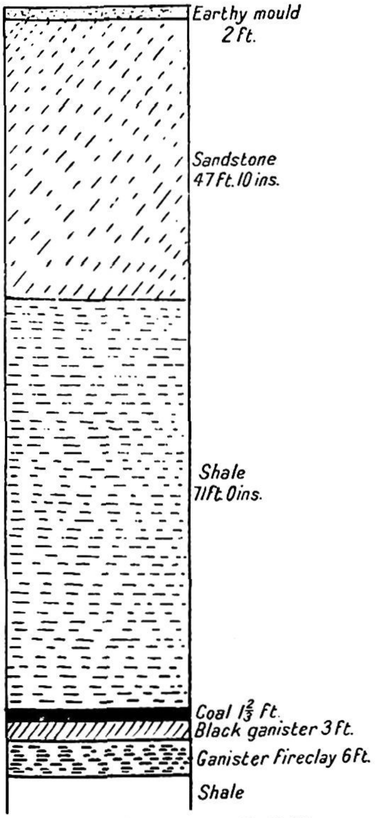

Fig. 28.—Section near Sheffield.

The deposit also extends northwards towards Huddersfield and Leeds, but as a distinct bed, becoming softer and more argillaceous, and forming a siliceous clay of inferior value, the fracture being less cherty and the grains produced by grinding are less angular, so that they do not produce such good bricks. Tourmaline seems to occur fairly abundantly, as do rutile, anatase, and brookite. The rocks also contain more felspathic material and white mica. Iron compounds are comparatively common in the cement.

The ganister deposit also extends southwards into Derbyshire, where it becomes more siliceous. Near Ambergate, the ganister beneath the Alton coal is 2 to 4 feet thick, and consists of subangular grains from 0·1 to 0·3 mm. diameter. A small quantity of heavy detrital minerals occur.

The Yorkshire ganister bed also appears to be continued into Lancashire, where, in the south of the country, it occurs beneath the Ganister coal. It is not equal in quality to the Yorkshire ganister, but is worked to some extent near Bolton, Wigan, Oldham, and the borders of Cheshire.

The "ganister" below the Ganister coal in North Lancashire is of poor quality, the average silica content being less than 85 per cent. It is obtained to some extent near Blackburn and Accrington.

Bastard ganisters are often used in place of the true ganister, and whilst they resemble the latter in chemical composition, they do not possess the same physical texture, and should be termed "silica rocks."

It is very difficult to distinguish some of the bastard ganisters from the true ones with the unaided eye, as both may be fine-grained and contain abundant traces of fossilised roots and other remains of plants. The difference is, however, readily seen when a thin section of the rock is examined under the microscope (see p. 137).

Omitting the numerous quartzites, quartz schists, or granulitic quartzose rocks which are sometimes—though erroneously—termed "ganister," the most important bastard ganisters occur in Durham and North-eastern Yorkshire, South Wales, Lanarkshire (Scotland), and at Ballyvoy, near Ballycastle (Ireland).

In North Yorkshire and Durham there are at least fifteen rocks which are used—together with fireclay—for the manufacture of silica bricks. They occur in various geological formations from the Lower Jurassic beds to the Upper Carboniferous Limestone. The topmost beds occur in the Moor Grit of the Inferior Oolite at Commondale, the "Hard Ganister" being used for silica bricks and also being ground for furnace linings. At the base of the Inferior Oolite is a bastard ganister termed "Pencil Ganister," consisting of a fine-grained silica rock containing a small proportion of mica, iron, and carbonaceous material. A bed of this rock about 3 feet thick occurs at Commondale, Yorkshire, beneath a thin coal, but it is impure, and contains numerous rootlets. It is not used to any great extent for silica bricks.

A few feet from the base of the Lower Coal Measures is a bastard ganister mined at Byerley House, Knitsley Fell, and Saltley. It is a fine-grained, white or greyish rock, 2 feet 6 inches to 9 feet in thickness, and consisting of angular grains varying between 0·05 and 0·15 mm. diameter. The rock is used for silica bricks and, combined with fireclay, for ganister bricks.

TABLE XXXIX.—ANALYSES OF KNITSLEY GANISTERS.[1]

	Pencil.	Shipley Moss.	Todds.	West Shipley.
Silica	99·34	97·53	97·65	97·22
Ferric oxide	0·06	0·25	0·07	0·25
Alumina	0·19	1·04	1·38	1·44
Titanium oxide	0·17	0·25	0·25	0·33
Lime	0·05	0·15	0·08	0·07
Magnesia	0·01	0·03	0·02	0·02
Loss on ignition	0·14	0·72	0·47	0·60
Fusion point	1810° C.	1810° C.	1790° C.	1790° C.
Seger cone	37	36–37	36	36

A number of bastard ganisters occur in the Carboniferous Limestone of Durham and North Yorkshire. The Egglestone ganister occurs just below the base of the Millstone Grit, and a pencil ganister occurs about 380 feet

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[1] Supplied by Knitsley Refractory Products, Ltd.

below the grit. It occurs in beds up to 10 feet thick at Rookhope in Weardale, where it is used for silica bricks. Some distance lower, lies the Nattrass Gill bastard ganister, below the Undersett Limestone at Wearhead and Wensley.

The ganisters of North Yorkshire and Durham have a rather larger proportion of impurities than the " true ganisters," and are a little higher in alumina. The alkalies are about the same, and consist approximately of equal parts of soda and potash with, if anything, a rather larger proportion of potash.

None of these " ganisters " possess the same fineness of grain or such density and hardness as the blue and black ganister of South Yorkshire, though a few rocks possess somewhat similar characteristics. Though the deposits are not of such high quality, they occur in ample quantity and are largely used.

The Crowstones of Cheshire have been worked for bastard ganister at Congleton Edge, Gun Hill, and Mossley. At the last-named place, the material closely resembles the true ganister of the South Yorkshire district. Irregular ganisters also occur associated with fireclay beneath the Crabtree coal near Froghall.

The Cumberland bastard ganisters are of inferior quality, usually occurring associated with fireclay chiefly near the base of the Middle Coal Measures.

A bastard ganister of poor quality occurring at the base of the Lower Coal Measures is found in the Forest of Dean, and is sold for ground ganister. It is very coarse, the average size of the grains being 0·3 mm. diameter.

A white bastard ganister (about 5 feet thick) occurs at Trevor, North Wales, in two beds below the Chwarele coal in the Lower Coal Measures.

The bastard ganisters in South Wales in the basal beds of the Millstone Grit are really quartzose sandstones, but they are used as ganister mixtures.

The Scottish bastard ganisters also occur in the Millstone Grit rocks, and are usually lower in silica than English ganisters, the average silica content being 90 to 95 per cent. together with up to 2 per cent. of alumina. The principal beds occur in association with the Top and Bottom fireclays, and are called Top and Bottom ganisters respectively. They are not really ganisters, but light-coloured and fine-grained sandstones with a partially siliceous bond. They contain a small amount of mica and felspar together with a variable proportion of ferruginous matter. Ganister-like sandstones also occur in the Millstone Grit and Carboniferous Limestone in Peeblesshire, Lanarkshire, Edinburghshire, Haddingtonshire, and Ayrshire, but are not worked to any great extent.

A siliceous sandstone lying immediately above the main seam of the Lower Fireclay is used to a limited extent in the manufacture of " ganister " bricks at Glenboig. At Gain, where it separates the " white " or main seam from the " blue clay," it varies from a mere rib to a bed 12 feet in thickness. At Heathfield, Garnkirk, a siliceous sandstone, 22 fathoms above the fireclay, is used, with an admixture of fireclay, in the production of " silica " bricks. At Castlecary a white ganister lower in the sequence, and only separated from the base of the series by a few inches of blaes, is also used.

Bonnybridge is the only locality where ganisters are worked in association with the Upper Fireclay ; there they are generally light-coloured, fine-grained, rooty, and somewhat micaceous. The texture is fairly uniform and the grain varies from 0·75 to 0·1 mm. Angular quartz forms the bulk of the rock, with a fair quantity of white mica ; the matrix is partly siliceous, partly argillaceous. The Bonnybridge ganisters, as compared with English ganisters, which they approach very closely in some respects, have a less purely siliceous centre and a slightly higher percentage of alkalies and lime.

In addition to the rocks of Millstone Grit age, a ganister lying immediately below the Gair or Calmy Limestone of the Upper Group of the Carboniferous Limestone series is now worked at Auchenheath, West Lanarkshire. The rock occurs in two beds, separated by a thin fireclay which is mixed and ground together with the two siliceous rocks.

A rock in association with the lowest limestones of the Carboniferous Limestone series at Carlops and Macbiehill in Peeblesshire, at Middleton and Vogrie near Gorebridge, and at Chapel Point, a few miles east of Dunbar, is between 2 and 3 feet in thickness and has a very high silica percentage.

A ganister much in the same stratigraphical position, found near Blackwood, in Lanarkshire, on the west side of the Clyde Valley, has attracted attention.

Several other sandstones of Carboniferous age in different localities in Lanarkshire, Midlothian, Dumfriesshire, Ayrshire, and Arran have also been suggested as possible sources of refractory material, and a good many of these have been analysed.[1]

From the foregoing statements it will be seen that whilst there are many silica rocks, there are few deposits which are commercially valuable as "ganister," and that this term relates principally to siliceous rocks having a special texture. This is primarily due to the fine angular grains of which the true ganisters are composed; but these grains have also been subjected to various influences, which have brought about important metamorphic changes and have surrounded the grains with an almost pure siliceous cement. In other words, the value of ganister as a refractory material does not lie in its geological location or in the rocks with which it is associated, but in the smallness and angularity of its grains, the manner in which they fit into each other, and the colloidal cement which unites them. This cement—like clays and colloidal silica—readily absorbs dyes such as malachite green or fuchsine, so that true ganisters are readily distinguished under the microscope.[2]

It is generally thought that ganister has probably been formed by the weathering of sandstone containing clay, followed by a prolonged process of cementation.

Ganister differs from crushed silica rock inasmuch as it can be made into bricks without any addition other than that of water. This property is due to the great angularity of its particles.

The following table shows the composition of five typical ganisters:—

TABLE XL.—ANALYSES OF GANISTERS.

	Hard Ganister.	Soft Ganister.	Lowood, Sheffield.	Bonnymuir.	Holling, Sheffield.
Silica	97·9	88·4	88·4	97·8	89·2
Alumina	0·6	6·4	7·0	0·2	4·0
Iron oxide	0·3	1·7	2·0	0·2	2·6
Lime	0·6	0·7	0·2	0·4	0·4
Magnesia	0·2	0·4	0·1	0·4	..
Potash and soda	..	..	..	0·2	0·4
Water, etc.	0·4	2·4	2·3	0·7	3·4

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[1] See *Special Reports on the Mineral Resources of Great Britain*, 1918, **6**.

[2] See footnote (3) on p. 167.

The best qualities of ganister have all the characteristics of cement quartzites, together with a feeble plasticity.

Though commonly regarded as a "clay," ganister is not correctly so described, as it is most closely related to the sands and gritstones. The composition of ganister should be within the following limits: silica, 87 to 99 per cent.;[1] alumina, 2 to 5 per cent.; ferric oxide, 0 to 1·5 per cent.; lime and magnesia, 0·25 to 0·75 per cent.; alkalies, 0 to 1 per cent.; otherwise it will not be sufficiently refractory. The selection of the ganister must, therefore, be made with great care.

Ganister is either quarried or mined according as it is worked at the outcrop or nearer the centre of the bed. Where it can be quarried, it is drilled and blasted by explosives, the broken rock being afterwards removed by hand or by means of some mechanical device such as a steam grab or shovel. Several old roadstone quarries are now being worked for ganister, but much of it is only bastard material. The Peak district pocket ganisters are quarried like sand-pits.

When ganister is mined in England it is worked either by the "pillar and stall" or "long wall" methods, but the Scotch ganisters are usually mined by the "stoop and room" method. In either case, the ganister is removed through the same shaft as the coal; it is then tipped until required. Very little has been done to increase the production of ganister, as the selling price of the material does not encourage the installation of more efficient machinery for working it. On this account, mechanical drills are only rarely employed, though more have been used during the past six years than formerly.

After mining, the ganister is reduced to a coarse powder without weathering. Both dry and wet methods of grinding are employed, but the former is gradually being superseded by the latter on account of recent Government regulations. In some cases, lime-cream is added during grinding; this addition is in all cases kept within narrow limits, and is only made when the material is deficient in binding qualities. In some works, 25 to 30 per cent. of fireclay is added during the grinding. Further information is given in the section on the manufacture of silica bricks (Chapter III.).

Some firms store the ganister-paste before moulding it.

Effect of Heat on Ganister.—The effect of heat on ganister resembles that on other forms of silica, though there are slight differences in the behaviour of silica obtained from various sources. According to Houldsworth and Cobb,[2] *Meanwood ganister* when heated without any bond shows a very large, but steady, expansion from 15° to 500° C., a still greater rate of expansion from 500° to 600° C. (associated with the inversion of β-quartz into α-quartz), followed by a slight contraction from 900° to 1000° C. On cooling, this ganister expands slightly from 1000° to 600° C., then there is a very rapid and large contraction from 600° to 550° C., followed by a steady contraction. The final effect is a permanent linear expansion of 0·7 per cent.

On reheating the ganister, the temperature-expansion graph has the same character from 15° to 600° C. as on the first heating, but the actual expansion is only about two-thirds as much. From 600° to 1000° C. there is a slight but steady contraction. The cooling curve does not differ appreciably from the heating curve, but from 400° to 15° C. the contraction is less than the expansion, so that a further permanent linear expansion of 0·08 per cent. is shown. No marked discontinuities in the temperature-expansion curve were noted about 100° C., or at 200° C. to 280° C.—which would indicate the

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[1] Best Yorkshire ganisters contain 95 to 96 per cent. silica.

[2] Houldsworth and Cobb, *Trans. Cer. Soc.*, 1921–1922, **21**, 227–276.

presence of tridymite or cristobalite in appreciable amount—so that the large permanent expansion obtained when the ganister was first heated cannot be ascribed to the transformation of quartz into tridymite or cristobalite. The very small change in the true specific gravity of the raw ganister after three heatings to 1000° C. indicates that very little or no transformation of the quartz takes place. But the porosity of the ganister is increased from 14·4 to 17 per cent. on heating, which is more than sufficient to account for the observed increase in length. The increase in dimensions of the ganister on heating to 1000° C. is due to an increase of porosity resulting presumably from a rearrangement of the quartz particles. This is important to makers and users of all bricks made from quartzitic material.

On firing Meanwood ganister without bond to Cone 9 (actually 1170° C.) repeated or subsequent heating to Cone 14 (1410° C.) for two hours causes only a small part of the quartz to be converted into cristobalite; no tridymite is produced. On subsequently firing to Cone 20 for two hours, the whole of the quartz is transformed into cristobalite and tridymite, the former being much in excess.

Meanwood ganister with lime bond, previously unfired, when heated shows a large expansion up to 500° C., a much greater rate of expansion between 500° C. and 600° C., a slight expansion at 600°–800° C., and a slight contraction from 800° to 1000° C. On cooling there is little change above 600° C., but a large and rapid contraction takes place between 600° and 550° C. (though not nearly so large as the expansion on heating), followed by a steadier but diminishing contraction down to 15° C. and leaving a permanent linear expansion of about 0·6 per cent. On a second heating each of the three temperature-ranges shows much less expansion than before, and a further small reduction of the expansion occurs on a third heating. A permanent expansion of 0·03 per cent. occurs after the second and third heatings. The porosity increases by about 4·5 per cent. as a result of the heating; this would account for the permanent change in dimensions without any conversion of the quartz. A sample previously fired to Cone 9 showed between 15° and 500° C. little more than half the increase in length observed for the unfired specimen. The rapid expansion from 550° to 600° C. was less than half that of the unfired specimen, although there was no sudden expansion at about 100° and 200° C., such as might be expected if tridymite or cristobalite were present in quantity. The specific gravity was now 2·60, and microscopic examination showed that the material consisted of quartz with a very small amount of cristobalite.

The heating of Meanwood ganister with a plaster bond to successive higher temperatures up to Cone 9 resulted apparently in a decreased expansion between 550° and 600° C. without indications of the formation of tridymite or cristobalite in quantity. The same sample (fired to Cone 9) after a subsequent firing to Cone 15 gave a heating curve which showed a smaller expansion between 550° and 600° C. and between 15° and 550° C. (than immediately after firing to Cone 9). From 600° to 1000° C. a slight expansion occurred instead of the contraction previously noted, the specific gravity was 2·49 and the refractive index showed that the specimen contained quartz and cristobalite, the quartz being in excess. After a further heating at Cone 19, the expansion on a second heating from 100° to 250° C. was almost doubled, the coefficient of expansion from 250° to 550° C. was small but regular, the discontinuity from 550° to 600° C. was slight, and from 600° to 1000° C. there was a small but regular expansion. The cooling curve was similar to the heating curve.

The forms of the curves obtained suggest that heating from Cone 15 to

Cone 19 caused a rapid conversion of the ganister to cristobalite and not tridymite, but that with ganister and plaster, tridymite may be formed in some quantity along with cristobalite.

The second heating curves for the test-pieces fired to Cones 15 and 19 differed considerably from the first heating curves between 15° and 250° C. The α- to β- tridymite or cristobalite conversion was not very noticeable on the first heating, though clearly seen on cooling and on subsequent heatings. This phenomenon is important and was observed repeatedly.

The bond material appears to cause a delay in the expansion effect, and in the formation of the cristobalite crystals.

In the case of a ganister bonded with plaster and fired to Cone 6 or to Cone 9 the change in dimensions was greater on cooling than on heating, but ganister without bond fired repeatedly at Cone 9 gave heating and cooling curves which practically coincided. Fireclays containing free quartz showed a similar difference between heating and cooling curves, fluxes being present with the quartz both in the fireclays and in the ganister bonded with lime.

Ganister bonded with clay needs more firing than with lime.

Uses.—Ganister is used for a variety of purposes. *Lump ganister* is the most coarsely crushed ganister rock, which is only used for rough work. *Ground ganister*—mixed with the requisite quantity of water—can be used in any form of furnace construction which will permit the material being rammed around a pattern or used in the form of a brick. It is largely used in iron-melting cupolas, Bessemer converters, and crucible-steel furnaces, and as a moulding sand by steel manufacturers. *Ganister bricks* are moulded out of a paste made by mixing ground ganister and water and then burning the bricks. They are sometimes sold as " silica bricks," though this term is also used to include bricks made of any siliceous material. There is also a number of patent refractory bricks composed of silica rock or sand to which 10 per cent. or more of clay has been added in order to produce a material with a composition similar to that of natural ganister but higher in alumina and, therefore (theoretically), more refractory. *Ganister mixture, pug-ganister* or *compo,* is a plastic refractory material consisting of a mixture of ganister and 5 to 20 per cent. of fireclay. It is used for lining furnaces and for general foundry use. It is also a popular material for patching and repairing kilns, furnaces, cupolas, etc. (see " Tamped Linings," Chapter XVIII.). Unfortunately, some firms supplying "ganister mixture " do not confine them to the use of true ganister but use other siliceous rocks—some of them of very inferior quality—whilst others use crushed quartz or white sand. *Puramachos* is an artificial ganister of this type, and consists of powdered quartz with 10 per cent. of clay and a little water-glass, but this material appears to vary greatly in composition.

Owing to its lack of plasticity, ganister cannot be made into such large blocks as are produced from fireclays.

It would be much better if the term " ganister " were restricted to the true ganister rock, and cements and compositions of other siliceous materials were referred to as *silica cements.* They could then be quite properly made of ground ganister, silica rock, sand, or any other convenient form of silica, together with a bonding agent such as fireclay or water-glass or other suitable material.

Firestones are porous silica rocks capable of withstanding a large amount of heat, and are used in place of firebricks of low grade. The term "firestones" is sometimes applied to a low grade of ganister. Rocks suitable for use as firestones occur in many localities, but two are used on a sufficiently large scale to merit special mention. The first is a fine-grained sandstone occurring in the

Upper Greensand in Surrey. It is usually calcareous, and contains about 40 per cent. of fragmentary colloidal silica, so that it is not highly refractory. The second is a similar stone, known in Hampshire as *malm rock*—a name which must on no account be confused with that applied to calcareous brick earths. Some limestones are also known as firestones, and serve admirably for oven plates, lining small lime kilns, and other purposes where no great refractoriness is required.

White sands are used for the inner lining of Siemens steel furnaces. They are obtained from a variety of sources, and so long as they are sufficiently pure to resist the action of heat and slags their source is unimportant. These sands are usually quartzitic.

Belgian silver sand is largely used for this purpose, but sand from Leighton Buzzard, Caldwell, Haydon Bridge, Huttons Ambo, Kings Lynn, and Aylesbury have also been used, and sea-sand has been used for lining copper smelting furnaces. Ground silica rocks from various sources may also be used satisfactorily, provided they are not too coarse and that the grains are not too uniform in size. The sands or ground rock should contain at least 95 per cent. of silica, not more than 0·5 per cent. each of iron oxide, lime, magnesia, and alkalies; they should not be wholly free from fluxes, as they must sinter sufficiently to remain in position when the furnace is in use. The purest sands can be used satisfactorily, if care is taken in working the furnace the first time the repaired hearth is used, as the slag which penetrates the hearth soon binds the particles of sand together.

Coarse particles are objectionable, as they make the laying of the hearth much more difficult, and, if present, should be removed by passing the sand through a 25-mesh sieve, though sands containing 40 per cent. of material retained on a 6-mesh sieve have been used satisfactorily.

Refractory sands for lining furnaces should have the same general characteristics as the crushed materials used for silica bricks (see Chapter III., also " Tamped Linings " in Chapter XVIII.).

Ground silica rock is sometimes sold as " white sand " (see also " Tamped Linings," Chapter XVIII.).

Most sands can *not* be used for the production of *best* silica bricks, for they lack the necessary tridymitic or cementitious structure.

The impurities in silica rocks are similar to those in clays, except that clay is itself an impurity in silica rocks, though welcome to a limited extent in ganister. The principal impurity found in silica rocks is iron oxide, the greater proportion being in the ferric state, but in some cases chalybite (ferrous carbonate) is present. Various alumino-silicates may be present, chiefly in the form of felspars, micas, and kaolinite or clay. Mica frequently occurs in foliated quartzites along the lines of foliation. Both potash and soda-lime felspars occur, and lime may also be present in the form of calcite, dolomite, or calcium phosphate. A small quantity of hydrous sodium silicate sometimes occurs in association with the secondary silica cement, introduced probably by an alkaline solution some of which was retained by the silica in the form of silicate of soda. Magnesia may occur as dolomite or as a ferromagnesian silicate such as serpentine, this latter, however, being very infrequent. Titanium occurs to a limited extent as rutile, brookite, or anatase, the first and third occurring in characteristic needle-like crystals, whilst brookite occurs in large flakes surrounded by minute secondary crystals in the cementing silica. Where the proportion of titanium is high it is generally present in this form, it having probably been deposited from solution simultaneously with the cementing silica. Zirconium occurs as zircon in minute crystals, generally in negligible proportions.

Grey quartzites occur in the Carboniferous system as a result of the admixture of very finely divided carbonaceous matter. Chlorite and other impurities may be present in some cases and so impart their characteristic colours to the quartzite.

The cementing material of silica rocks is very variable in composition, and this material, when fired, determines the changes that are necessary for the formation of a sound silica brick. An undue proportion of binding material in a quartzite is undesirable, as it renders the brick unstable on heating and less refractory.

It is important to remember that a small percentage of alumina, potash, and certain other elements may represent a much larger proportion of impurity. Thus, 10 per cent. of felspar would only show 1·6 per cent. of potash and 1·8 per cent. of alumina, the remaining 6·6 per cent. being silica, which is included in the total silica. Hence, a material appearing to contain only 3·4 per cent. of impurities may actually contain 10 per cent. For information on the effect of heat on siliceous mixtures see pp. 34, 82, 184 *et seq.*

Most of the impurities are incapable of removal by commercially remunerative methods, so that the only way is to discard those portions of the material which are too impure to be used with safety. Generally speaking, a silica rock to be useful for refractory purposes must contain at least 97 per cent. of silica, though some excellent ganisters contain less than 90 per cent. The metallic oxides other than alumina should not exceed 5 per cent.

The chemical and physical properties of the highly siliceous rocks depend largely on the proportion of silica present. As most of these rocks contain 90 per cent. or more of silica, the properties of all of them are considered on p. 154 *et seq.*, special variations (as in the case of ganister) being mentioned as they occur.

Diatomaceous earth or Kieselguhr (sometimes known as **Barbadoes earth**) is a highly siliceous residuum left by the decay of extremely minute plants (diatoms) having an external casing of silica. In time, the accumulation of countless millions of these microscopic siliceous shells forms a bed of a light porous nature varying in colour from an almost pure white to a dark brown, due to various organic and inorganic impurities which may be present. The deposits are usually more or less contaminated with other materials which have been deposited simultaneously, the principal impurities being silt, clay, sand, volcanic ash, and decayed organic matter. With the exception of the organic matter, which is destroyed by calcining the material, these impurities cannot be separated cheaply and, therefore, affect the value of the kieselguhr. There are, however, very pure beds of kieselguhr which contain 95 per cent. and more of silica in Germany, Norway, the United States, Italy, and near Algiers.

The chief English deposit of diatomite is in Kentmere Valley near Lake Windermere, where it covers about 100 acres and is about 15 feet thick.

The German kieselguhr is obtained chiefly from Naterleuss, between Hamburg and Hanover, where a deposit 150 feet thick occurs, its colour varying from white at the surface—where it is associated with a coarse sand which can be removed by washing—through a bed of grey material containing less sand and enough carbonaceous matter to calcine the material, to the lowest bed which is 50 to 100 feet thick, and consists of green kieselguhr containing up to 30 per cent. of carbonaceous matter. Important deposits from which large supplies have been obtained also occur at Oberhohe.

The Algerian beds are amongst the finest in the world, though, as yet, they have not been fully exploited.

Enormous beds occur at St Lucian, sometimes attaining a thickness of 150 feet, the better qualities occurring near the bottom of the deposit.

Other smaller or less pure deposits occur in France, Spain, Ireland, and Scotland, though a deposit of good quality occurs at Auxillac in France, an analysis of which is given below. The Irish kieselguhrs are coloured and of limited usefulness. In Scotland (Isle of Skye) kieselguhr occurs in association with peat in beds up to 40 feet thick, but it is not of first-class quality.

There are over 8000 varieties of diatoms, varying greatly in size and shape; some of them are highly intricate structures. The impurities present are usually clay, quartzose sand, and vegetable matter. The greater part of these impurities can be removed by washing, but great care is needed not to break down the diatoms—most of which are, individually, very fragile. The heat-insulating value of broken diatoms is much less than that of whole ones. The vegetable matter present is generally destroyed by calcining the earth at a bright red heat in a gentle current of air.

Valuation.—The identity and commercial value of various diatomaceous earths are judged from:

(i) a microscopical examination, which enables the diatoms to be readily distinguished;

(ii) the volume-weight of the material in the form in which it is offered for sale;

(iii) the proportion of diatomite present;

(iv) the wholeness or otherwise of the diatoms;

(v) the porosity of the material;

(vi) in the case of raw material, the effect of heating to 900° C. or above. Kieselguhr, when pure, is not affected by heating up to 1300° C., but most commercial samples sinter badly and so lose their porosity at 1100°–1150° C. A microscopical examination of the heated material is desirable, as well as a determination of the refractoriness.

The colour of kieselguhr varies very considerably and does not indicate the quality of the material; the best qualities are almost pure white. Table XLI. shows the composition of kieselguhr from various sources.

TABLE XLI.—ANALYSES OF KIESELGUHR (A. BIGOT).

Composition.	Lünebourg.	Auxillac.	St Denis le Sig.		Lompoc, California.		
			A.	B.	A.	B.	C.
Combined water	5·26	3·50	6·40	5·20	5·54	5·57	2·22
Organic matter	8·43	3·00					
Silica	81·25	88·90	74·00	86·50	88·78	85·28	94·59
Alumina	3·19	2·65	1·99	1·35	2·68	5·35	1·87
Ferric oxide	1·34	1·50	1·06	0·50	trace	1·12	0·76
Titanium oxide	0·15	0·26	..	..	0·10	0·21	0·10
Lime	0·18	0·20	6·61	2·95	1·61	1·12	0·83
Magnesia	0·20	0·15	1·58	0·75	1·30	1·30	trace
Alkalies	..	..	2·16	0·40	..	..	..
Carbon dioxide	..	..	6·20	2·70	..	..	..
					white	brown	white compact shale

In its pure state, kieselguhr contains 25 to 45 per cent. of moisture which is expelled at 100° C., and is a very light, soft, easily abraded material. The silica in diatomaceous earths is in a very peculiar state, as it is in the form of an irreversible colloidal gel containing 5 to 10 per cent. of combined water which is evolved on heating to redness. In the raw earths, there is usually a variable proportion of reversible silica gel. These two forms of silica are easily attacked by hydrofluoric acid, and are soluble in solutions of sodium carbonate of all strengths.

On heating the kieselguhr to 600° C. to 700° C. in a current of air, the organic matter burns away, and whilst the appearance and volume of the earth remains unchanged (except for the colour), its power of absorption of gases and liquids is increased and it becomes harder. When heated between 700° C. and 1000° C., these earths contract and increase in hardness and apparent density. The cubical contraction increases fairly uniformly with the temperature of calcination, a block with a volume of 100 c.c. at 700° C. shrinking to about 25 c.c. at 1400° C. to 1600° C. The apparent density—or, strictly, the volume-weight—remains constant at 0·5 to 0·7 below 700° C., rises rapidly to 1·4 at 1100° C. to 1400° C., and steadily increases to about 2·2 at 1400° C. to 1600° C., between which temperatures the material fuses. The true specific gravity is about 2·60 below 1000° C., but at the fusion-point it falls to 2·22 to 2·35. About 77 to 80 per cent. of the total volume of dried material consists of air; this proportion of voids is 6 to 8 times that in lightly calcined clays. The normal melting-point is 1570° C. to 1600° C.,[1] but it is sometimes as low as 1300° C. in very impure earths.

Kieselguhr possesses certain catalytic properties, though they are less marked than those of freshly deflocculated china clay.

The thermal conductivity of the calcined material is proportional to its volume-weight. Its value as an insulator in comparison with other materials is shown in the following table of thermal conductivities:—

TABLE XLII.—THERMAL CONDUCTIVITIES.

Substance.	Temperature. °C.	Thermal Conductivity in Gm. Cals. per Sq. Cm., per Cm. per Sec., per 1° C.
Kieselguhr	100 to 900	0·00018
Fireclay brick	200 „ 1000	0·00420
Silica „	150 „ 1000	0·00200
Magnesia „	700 „ 1400	0·00910
Bauxite „	200 „ 1000	0·00330
Graphite „	1000 „ 1200	0·02500

At 2000° F. (1093° C.) one thickness of raw kieselguhr is equivalent to 6·5 of good fire bricks or 1·35 to 1·65 of magnesite bricks.

The specific heat of kieselguhr resembles that of ceramic materials and averages about 0·25, so that a compacted mass of the material with a volume-weight of 0·5 absorbs 2½ times as much heat as the loose powder with a volume-

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[1] Kanolt found that the average melting-point of the American silica bricks he tested was 1700° C. Seger found an even higher figure (Table XLIII.). According to Endell and Ricke, the melting-point of pure quartz is only 1470° C. if the temperature is raised so slowly that the conversion into tridymite is complete. Under the ordinary rates of heating (about 5° per minute), the conversion is only slight, and a much higher melting-point is recorded.

weight of 0·2, whilst a fireclay brick with a volume-weight of 1·8 will absorb 9 times as much heat as the powdered earth.

The chief uses of kieselguhr and other diatomaceous earths as refractory materials depend on their lightness and porosity, to which properties they owe their great heat-insulating power. They are, therefore, of great value in many situations where both refractoriness and heat-insulating properties are desired, but on account of their great porosity they are of no value for resisting the corrosive action of slags and fluxes, and should not be used in exposed positions in a furnace; if used as an intermediate walling, *i.e.* where the surface is protected by firebricks or other slag-resisting material on the one side and from the weather on the other, these earths are highly satisfactory insulators, and are largely used for this purpose in the form of thin bricks in kilns and furnaces. Loose kieselguhr powder is also used for the covering of the crowns of kilns and furnaces of various types. Thus, a tunnel-kiln efficiently insulated with kieselguhr on the sides and roof can usefully employ 88 per cent. of the available heat in the fuel, the outside walls having only a temperature of 28° C., when that of the inside walls is 1250° C.

For use, the kieselguhr is dug in such a way as to produce rough blocks, which are stacked in fields in the open and left until they contain only 15 to 25 per cent. of water. The half-dry material is then taken to the grinding plant, where it is reduced to powder, and may be dried still further by passing warm air through the grinder. Artificial drying does not appear to be profitable, though in California the blocks are exposed to the air 40 to 50 days, then sawn into bricks, and afterwards the drying is completed in kilns. If calcined kieselguhr is required, the grinding may be postponed until after calcination. The calcining is usually effected in small round kilns, but where the output is sufficiently large a continuous shaft-kiln is more economical.

For the production of insulating bricks, the crushed kieselguhr is mixed with sufficient clay to enable it to be made into bricks.

Moler is a material somewhat resembling kieselguhr, but is less refractory, as it contains a considerable proportion of clay and volcanic ash, for which reason it is self-binding and can be made into bricks without any other bond. It is found chiefly in Norway, and a typical analysis of this material, as used by Moler Products Ltd., is as follows:—

Silica (diatoms)	66·90	per cent.
Alumina	13·00	,,
Ferric oxide	6·90	,,
Lime	1·00	,,
Magnesia	1·66	,,
Sulphuric anhydride	0·25	,,
Alkalies	0·76	,,
Loss on ignition	9·85	,,
	100·32	

Moler bricks for heat-resisting purposes are made by mixing the material with water in a pug mill, shaping the bricks by hand in the same manner as fireclay bricks, and afterwards drying and burning them in a similar manner, but the finishing temperature is only about 1000° C. Owing to their fusibility, they must not be exposed to very high temperatures.

THE EFFECT OF HEAT ON SILICA MIXTURES.

The effect of heat on pure silica has been described on pp. 158–164. All the forms of pure silica are highly refractory and have a resistance to heat similar to that of Coal Measure fireclays (Seger Cone 35). The refractoriness of silica is, however, like that of the fireclays, greatly reduced by the presence of very small proportions of bases. It is important to observe that the addition of a highly refractory clay to silica produces a material of lower heat-resistance than either the clay or the silica separately. Seger found that a kaolin, when used alone, had a softening point corresponding to Cone 35, and pure quartz one corresponding to Cone 34. If these two substances were mixed together in progressively increasing proportions of silica, the fusibility of the clay gradually increased until a mixture containing 90 per cent. of silica was reached, when the mixture of maximum fusibility (Cone 27) was obtained, mixtures richer in silica being more refractory. If pure alumina is substituted for the clay the same phenomenon is observed (fig. 29). This is highly important to users of ganister and other siliceous rocks, as it shows that their refractoriness diminishes rapidly with small amounts of alumina, and that a mixture of such a material and clay containing only 80 per cent. of silica may be even more refractory than one containing 90 per cent. of silica. This fact has not yet been fully appreciated by many manufacturers of silica bricks.

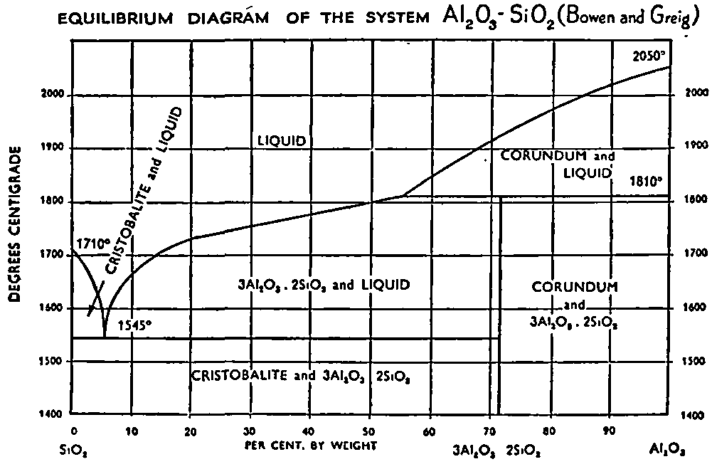

FIG. 29.—Refractoriness of mixtures of alumina and silica.[1]

It is particularly interesting to observe that a mixture of clay and silica corresponding in chemical composition and general properties to ganister has the lowest refractoriness of any possible mixture. This observation of Seger's has been repeatedly confirmed, and in connection with the extensive use of ganister in furnaces, it serves to show in a striking manner that refractoriness alone is not the prime factor in a furnace lining.

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[1] *J. Amer. Cer. Soc.*, 1924, **7**, 238–254.

The following table shows the melting-points of mixtures of silica and alumina, as determined by Seger, Hecht, and Simonis[1]:—

TABLE XLIII.—MELTING-POINTS OF ALUMINA-SILICA MIXTURES.

Molecular Composition.	Per Cent. Alumina.	Per Cent. Silica.	Melting-Point (Seger Cones).
Al_2O_3	100	..	42
$Al_2O_3+0{\cdot}13SiO_2$	92·9	7·1	41
„ +0·33 „	82·0	18·0	40
„ +0·66 „	71·9	28·1	39
„ +1 „	62·9	37·1	38
„ +1·33 „	56·0	44·0	37
„ +1·66 „	50·5	49·5	36
„ +2 „	45·8	54·2	35
„ +2·5 „	40·4	59·6	34
„ +3 „	36·1	63·9	33
„ +4 „	29·7	70·3	32
„ +5 „	25·3	74·7	31
„ +6 „	22·0	78·0	30
„ +8 „	17·5	82·5	29
„ +10 „	14·5	85·5	28
„ +13 „	12·8	87·2	+27
„ +15 „[2]	10·1	89·9	−27
„ +20 „	8·4	91·6	30
„ +23 „	6·5	93·5	32
SiO_2	..	100	35

The eutectic for mixtures of Zettlitz kaolin and silica is $Al_2O_3.12{\cdot}8SiO_2$, which has the same composition as the eutectic in the table (*cf.* figs. 29 and 30).

According to Flach[3] the eutectic between Zettlitz kaolin and silica is changed by the addition of a small amount of base. He found the following to be eutectics,[4] but did not publish the fusing-points:—

TABLE XLIV.—EUTECTICS OF KAOLIN WITH FLUXES.

Mixture of Kaolin with	Molecular Ratio.
5 per cent. $CsCO_3$ or $KNaCO_3$	$1Al_2O_3 : 9{\cdot}6SiO_2$
5 „ „ $MgCO_3$ or MnO	$1Al_2O_3 : 10{\cdot}6SiO_2$
5 „ „ Li_2CO_3	$1Al_2O_3 : 11{\cdot}5SiO_2$
5 „ „ Carbonate of Na, K, Cs, Co, Ni, Zn, Cu, Pb	$1Al_2O_3 : 12{\cdot}4SiO_2$
5 „ „ Rb_2CO_3, $FeCO_3$ or $Bi_2(CO_3)_3$	$1Al_2O_3 : 13{\cdot}3SiO_2$
10 „ „ $CaCO_3$	$1Al_2O_3 : 6{\cdot}2SiO_2$
10 „ „ $MgCO_3$ or MnO	$1Al_2O_3 : 6{\cdot}7SiO_2$
10 „ „ $SrCO_3$	$1Al_2O_3 : 7{\cdot}9SiO_2$
10 „ „ $BaCO_3$ or $CoCO_6$	$1Al_2O_3 : 9{\cdot}6SiO_2$
10 „ „ Carbonate of K, Fe, Ni, Zn, Cu	$1Al_2O_3 : 10{\cdot}6SiO_2$
10 „ „ Carbonate of Na, Rb, Cs, Pb, Bi	$1Al_2O_3 : 12{\cdot}4SiO_2$
10 „ „ Li_2CO_3	$1Al_3O_3 : 17{\cdot}4SiO_2$

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[1] *Sprechsaal Kalr.*, 1914, p. 158.

[2] Eutectic.

[3] *Sprechsaal Kalr.*, 1913.

[4] Numerous other eutectics are given on pp. 92–94.

TABLE XLV.—REFRACTORINESS OF LIME-SILICA MIXTURES.[1]

Molecular Ratios.		Mols. SiO_2 to 1 Mol. CaO.	Per Cent. CaO.	Per Cent. SiO_2.	Fusing-Point (Seger Cones).	
					Rieke.	Boudouard.
8CaO	$1SiO_2$	0·125	88	22	..	19
5 ,,	1 ,,	0·2	82·3	17·7	..	..
4 ,,	1 ,,	0·25	79	21	..	16–17
3 ,,	1 ,,	0·33	73·6	26·4	..	18–19
5 ,,	2 ,,	0·4	70	30	..	15
2 ,,	1 ,,	0·5	65	35	29	16–17
5 ,,	3 ,,	0·6	61	39	16	..
10 ,,	7 ,,	0·7	57	43	14	..
4 ,,	3 ,,	0·75	55·4	44·6	..	15
5 ,,	4 ,,	0·8	54	46	15–16	..
10 ,,	9 ,,	0·9	51	49	17	..
1 ,,	1 ,,	1·0	48·2	51·8	19	15–16
5 ,,	6 ,,	1·2	43·8	56·2	17	..
4 ,,	5 ,,	1·25	42·7	57·3	16–17	..
10 ,,	13 ,,	1·3	42	58	16	..
5 ,,	7 ,,	1·4	40	60	15–16	..
7 ,,	10 ,,	1·3	39·5	60·5	..	13–14
2 ,,	3 ,,	1·5	38	62	15	14–15
5 ,,	8 ,,	1·6	37	63	14–15	..
10 ,,	17 ,,	1·7	35·5	64·5	14	..
5 ,,	9 ,,	1·8	34	66	14	..
1 ,,	2 ,,	2	31·8	68·2	15	16
2 ,,	5 ,,	2·5	27	73	20–26	21
1 ,,	3 ,,	3	23·7	76·3	29	31
1 ,,	4 ,,	4	19	81	31	..
1 ,,	5 ,,	5	16	84	32	..
1 ,,	6 ,,	6	13·4	86·6	33	32–33
	Pure SiO_2	..	..	100	36	35

The very serious effect of lime on silica is often overlooked, but is clearly shown in fig. 30, which is a graphic form of Tables XLV. and XLVI.; it should be compared with fig. 12.

Philippi[2] obtained somewhat different results for the mixtures given in the following table:—

TABLE XLVI.—REFRACTORINESS OF CALCIUM SILICATES.

Molecular Ratios.	Fusing-Point (Seger Cones).
$2CaO.3SiO_2$	14
$CaO.SiO_2$	17–18
$4CaO.3SiO_2$	16
$2CaO.SiO_2$	40
$3CaO.SiO_2$	41

J. W. Cobb obtained the following results by heating carefully prepared mixtures:—

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[1] *Sprechsaal*, 1907, No. 44.

[2] *Ibid.*, 1908, No. 46.

TABLE XLVII.—REACTION TEMPERATURES OF BASES AND SILICA.

Molecular Ratios.	Reaction. Commences ° C.	Reaction. Complete ° C.	Product.
$1CaCO_3 + 1SiO_2$	800	1400	$CaO.SiO_2$ formed; soluble in acid.
$4CaSO_4 + SiO_2$	1005-1010	1350	
$1CaCO_3 + 10SiO_2$	800	1250	
$1CaSO_4 + 10SiO_2$	1000–1020	1300	
$3CaCO_3 + 1SiO_2$	800	1250	$2CaO.SiO_2$ formed.
$3CaCO_3 + 10SiO_2$	about 1000	1250	
$1Na_2CO_3 + 1SiO_2$	800	950	$Na_2O.SiO_2$ formed.
$1Na_2CO_3 + 10SiO_2$	800	1150	$Na_2O.4SiO_2$ formed; soluble in acid.
$1Na_2SO_4 + 1SiO_2$	1120	..	$Na_2O.SiO_2$ formed.
$1Na_2SO_4 + 10SiO_2$	1080–1100	..	
$1Na_2CO_3 + 1CaCO_3 + 10SiO_2$	800	1000	Insoluble in acid.
$1Na_2SO_4 + 1CaSO_4 + 10SiO_2$	930-950	..	
$1Na_2CO_3 + 1Al_2O_3 + 10SiO_2$	800	1000	
$1Na_2SO_4 + 1Al_2O_3 + 10SiO_2$	935–955	..	
$1CaCO_3 + 1Al_2O_3 + 10SiO_2$	800	1300	
$1CaSO_4 + 1Al_2O_3 + 10SiO_2$	1000-1020	1300	
$1Na_2CO_3 + 1CaCO_3 + 1Al_2O_3 + 10SiO_2$	800	1400	Insoluble in acid.

The chief investigations on the various lime-silica compounds have been made by Rankin and Wright,[1] who found that only four definite compounds can exist: (i) the metasilicate, $CaO.SiO_2$, stable up to 1500° C.; (ii) tricalcium disilicate, $3CaO.2SiO_2$, melting at 1475° C., or in the presence of $CaO.SiO_2$ at 1455° C.; (iii) calcium orthosilicate, $2CaO.SiO_2$ (in three forms); and (iv) calcium trisilicate. If alumina is also present there can be formed anorthite, $CaO.Al_2O_3.2SiO_2$ (1550° C.), gehlenite $2CaO.Al_2O_3.SiO_2$ (1590° C.) and numerous eutectics melting between 1165° and 1900° C.

For further information on the characteristics which determine the suitability or otherwise of silica rocks for the manufacture of refractory materials, see Chapter III.

Other properties of silica are conveniently considered in Chapter XV., dealing with "Fused Silica."

Asbestos is a term used to include the fibrous varieties of several silicates of one or more of the following metals: magnesium, calcium, sodium, and iron. There are five principal varieties of asbestos, the chief of which is *chrysotile*, which is highly valued on account of the strength and length of its fibres. It appears to crystallise in the orthorhombic system, and forms long, flexible fibres, having a specific gravity of about 2·5 and a hardness of about 4. Its colour varies from yellow or green to brown, and it has a refractive index of 1·57, a birefringence of about 0·01, and a straight extinction between crossed nicols. It is readily dissolved by hydrochloric and sulphuric acids.

Chrysotile is found chiefly in the eastern parts of Quebec in association with rocks of pre-Cambrian and Ordovician age, and appears to have been formed by the alteration of peridotite or olivine rock. It also occurs in Vermont, U.S.A., in beds which are a continuation of the Canadian deposits, in the Ural Mountains (Russia), and in Rhodesia (Africa).

Tremolite is a double silicate of calcium and magnesium. It usually occurs

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[1] *Amer. J. Sci.* (4), 1915, 39, 4–10, 40.

in a state of great purity, being very low in iron. It is more loosely aggregated than chrysotile, and is of a white or greyish colour, with a hardness of about 5·5 and a specific gravity of about 3. Its refractive index and birefringence are very high, being 1·636 and 0·028 respectively. Tremolite is rather more fusible than chrysotile. It is not decomposed by any ordinary acids. It is principally obtained from Lombardy and Piedmont, where it occurs in association with talc and mica schists.

Crocidolite is a double silicate of sodium and iron, which is not of great importance for refractory purposes on account of the large proportion of iron it contains. It is of a bluish colour, and has a refractive index and birefringence closely approximating to that of tremolite, whilst its hardness is about 4 and its specific gravity about 3·2. It is found chiefly in Griqualand West, South Africa, in a green slaty rock of early Palæozoic or pre-Cambrian age.

Anthophyllite is a double silicate of magnesium and iron, and has a hardness of 5½ and a specific gravity of about 3·1. It is of a grey or brown colour, having

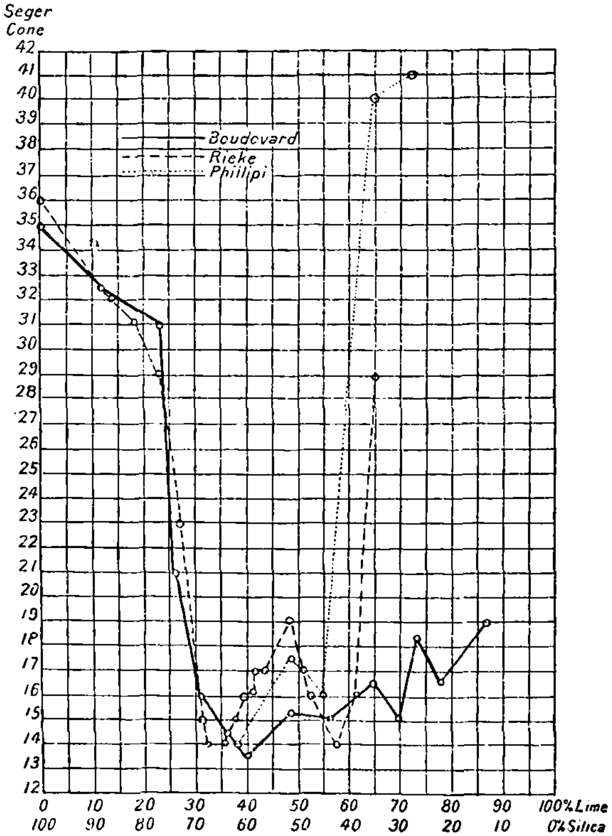

FIG. 30.—Refractoriness of mixtures of lime and silica.

a refractive index of 1·63 and a birefringence of 0·024. Anthophyllite is not decomposed by any ordinary acids. It is found principally in Georgia, U.S.A., in talc and tremolite schists, and in gneiss.

Amosite is a ferrous silicate containing about 39 per cent. of iron oxide with a small proportion of magnesia. It consists of fibres (often 4 to 7 inches in length) which are grey or green when fresh, and brown when weathered. It is found chiefly in banded siliceous ironstone in N.E. Transvaal.

Asbestos is not very refractory, but it is used in some refractory materials, including asbestos bricks and the " fuel " for gas stoves. It is also sometimes used in refractory cements.

NEUTRAL REFRACTORY MATERIALS.

The chief neutral refractory materials are—

1. *Carbon.*
2. *Carbides* (including carborundum).
3. *Chromite.*

Carbon is an element which is stable at all temperatures up to 500° C. in the absence of air. Above this temperature it is converted very slowly into graphite, except in the presence of catalysts such as silica, alumina, iron, lime, or boric oxide, when the action takes place much more rapidly. In the presence of air carbon burns, and it is wholly converted into a gas, which may be either carbon monoxide or dioxide according to the conditions of combustion.

The carbon employed in the manufacture of refractory goods is generally used in the form of *graphite* or *plumbago*, which are naturally occurring varieties of carbon, but *coal*, *coke*, *tar*, and *sawdust* are also used in the manufacture of refractory goods. The carbon protects the clay from the heat and enables the goods to stand sudden changes in temperature.

Plumbago, black lead, and **graphite** are three names for the same substance, and all of them refer to a peculiar form of carbon found as a grey-black mineral which is not difficult to recognise.

Graphite is stable at all temperatures in the absence of air; if oxygen is present, the graphite combines with it at temperatures above 700° C.

Natural graphite occurs in two forms, viz.: amorphous[1] graphite and flake graphite.

Amorphous graphite occurs in Cumberland, Mexico, Czecho-Slovakia, Bavaria, Italy, Rumania, Spain, and Texas (U.S.A.). It is chiefly used for foundry work and lead pencils.

Flake graphite is found principally in Ceylon, Madagascar, Siberia, and Alabama, New Jersey, Pennsylvania, California, Montana, and Texas, in the United States.

English graphite is not necessarily that mined in this country, but merely that bought in London.

The greater part of the graphite used in this country is obtained from Ceylon and Madagascar. The American, Canadian, and Malagasy graphites are definitely laminated. Of the American materials, the Alabama flakes are usually the smallest and thinnest. The Pennsylvanian flakes are slightly larger and thicker, whilst the Canadian ones are still larger and more irregular. The Malagasy flakes are nearly twice as large as the American ones, and instead of being oval are polygonal. The Ceylon graphites are not really flakes in the same sense as the American and Malagasy ones, but consist of extremely thin rectangular or triangular grains; they have great covering power and a

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[1] The term "amorphous" carbon is probably incorrect, as the X-ray spectrum of many apparently amorphous forms of carbon shows them to be distinctly crystalline.

slow rate of burning. The Mexican and Montana graphites are of almost equal value.

The Ceylon graphite is the best for use in the manufacture of crucibles. Articles made with flake graphite are stronger and more durable than those made of graphite with angular grains (such as Ceylon graphite), but they have the disadvantage of being more subject to lamination; consequently, Ceylon graphite, or some of the more angular, prepared Canadian graphite, is preferred.

According to R. T. Stull and H. G. Schurecht,[1] flake graphite such as that found in Alabama can be greatly improved by mixing it with 15 to 20 per cent. of tar and making it into briquettes with a pressure of about 500 lbs. per square inch, baking the briquettes quickly at 1000° C., crushing, screening, and retaining the particles between Nos. 18- and 100-mesh sieves. The product, when mixed with ordinary crucible clays, etc., can be moulded readily, and is less liable than the flaky graphite to cause welding seams and laminations, but it does not appear to be so good as the best natural (Ceylon) graphite.

Artificial graphite is manufactured on a large scale (i) by heating anthracite or petroleum coke in an electric furnace similar to those used in the production of carborundum; (ii) by grinding a mixture of coke and tar or molasses, moulding and baking it in suitable ovens and afterwards "graphitising" the flakes in an electric furnace; and (iii) as a by-product of the manufacture of carborundum. The product is very pure—containing only about 0·1 to 0·2 per cent. of amorphous carbon and 0·1 to 0·5 per cent. of ash—the other impurities in the original material having been volatilised. This form of graphite is much more stable than natural amorphous carbon, and is capable of resisting sudden changes of temperature much more satisfactorily; but no form of artificial graphite yet made is as good for crucible manufacture as the best natural graphite.

An inferior variety of graphite is produced during the melting of iron in blast furnaces. It is termed *kish*, and accumulates near the base of the furnace, having been thrown out of solution from the molten iron.

The graphite which was originally the most extensively used as a refractory material, *i.e.* in the production of crucibles, was that obtained in Bavaria, but the quality of the Ceylon graphite is so superior that it has gradually displaced the Bavarian material in most parts of the world.

It is important to observe that the term "graphite" is applied to several forms of carbon which are by no means identical; from some sources, the graphite is crystalline and flaky, from others it is amorphous and friable, and from still others it is dense, hard, and resembles anthracite.

A method of recovering graphite from old crucibles which is largely used on the Continent is as follows: The crucibles must be carefully cleaned from adherent slag and other impurities of an adventitious character, crushed to powder, and the graphite removed by means of a vanning table or other form of separator. If the grinding is sufficiently complete, and the powder is treated in an air separator (fig. 42), it is not difficult to obtain a fairly pure graphite as well as a useful grog. This method of separation is based on the fact that the graphite will occur almost exclusively among the finest particles in the mixture.

Where an exceptionally high degree of purity is required, the graphite may be boiled with dilute hydrochloric acid and subsequently washed. This treatment is particularly effective in removing iron compounds, but it is costly.

The following are typical analyses of good graphite, the wide variations in samples from the same locality being very noteworthy:—

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[1] *J. Amer. Cer. Soc.*, 1919, **2**, 391–399.

TABLE XLVIII.—COMPOSITION OF GRAPHITE.

	Cumberland.		Bavaria.		Ceylon.		Canada.
Carbon . . .	82	92	81	66	68	99	79
Volatile matter .	5	1	8	1	5	..	2
Ash . . .	13	7	11	32	27	1	19

The graphite used for refractory purposes should contain at least 85 per cent. of carbon and preferably more than 90 per cent. ; it should be as free as possible from mica, pyrites, iron oxide, and other non-volatile impurities.

In preparing graphite for use as a refractory material, the pieces of graphite are freed from all other materials as far as possible ; they are then ground in a ball mill and sifted, the fine portion being used and the coarse material being reground. In order to avoid the loss of the dust produced by the foregoing treatment, it is usual to pass the finely ground graphite between closely set crushing rolls which compress it into flakes. Whilst both dust and large flakes should be avoided, the flakes used should be sufficiently large to unite satisfactorily with the clay or other bonding material. None of the flakes should pass through a 100-mesh sieve, and a number of them should be about 0·04 inch diameter. A mixture of flake and granular graphite is preferred by some crucible manufacturers.

The impurities in graphite are usually separated by grinding or by flotation where they are free and soft, but harder and interbedded impurities must be separated by the use of a burr-mill, which grinds the impurities much finer than the graphite itself; they are easily separated by subsequent screening. It is not usually difficult to obtain a product with over 90 per cent. of carbon.

Graphite is greyish-black in colour, with a metallic lustre and a hardness of about 1 on Mohs' scale. Natural graphite has a specific gravity of 2·01 to 2·58, and that made artificially has a specific gravity of about 2·01. By compression, the specific gravity can be raised to about 3·0. Graphite has a very low coefficient of expansion, viz. about 0·0000079 at 40° C. to 50° C. The specific heat is 0·200 at 61° C. and 0·252 at 138° C. ; the thermal conductivity is 0·012. It burns slowly when heated to a high temperature with sufficient oxygen or air, and leaves an ash containing most of its impurities. Where the proportion of ash is considerable, it may affect the refractoriness of the graphite, but in those graphites used for crucible-making, there is seldom sufficient ash to affect the crucibles at ordinary working temperatures, as the fluxing action is retarded by the formation of a dense skin due to the interaction of the clay and graphitic flux. Alabama graphite ash seems to have a smaller fluxing power than the ash of Ceylon, Canadian, Pennsylvanian, or New York graphites.

Graphite is insoluble in all acids. It is devoid of plasticity, and cannot be conveniently used alone, but as it has no apparent action on clay or slags, it may be used as a separating layer between the basic and acid portions of open-hearth furnaces. It is also mixed with the clay used for the manufacture of crucibles so as to render them less sensitive to sudden changes in temperature, to increase the transmission of heat to the contents and thereby the speed of melting metals, to produce a reducing atmosphere inside the crucible, and to give the crucible a smooth surface so that the contents will not adhere to it.

It is important that the right quality of graphite should be used. The best qualities have a flaky texture, burn very slowly, and are almost free from ash. Considerable skill is required in selecting graphite for crucible manufacture. The amorphous varieties of graphite are quite unsuitable; for this reason the Bohemian, Austrian, Italian, Korean, and Mexican graphites should *not* be used. The most suitable graphites are the so-called "crystalline" ones found in Bavaria, Ceylon, and Madagascar and some of the American graphites.

Pure graphite consists of a series of sheets of carbon atoms.[1] The forces holding the atoms together in the layers are stronger than the forces between the layers; this leads to a plane of cleavage and variations in the electrical conductivity in different directions. The sheets are 3·35Å apart. The softness of graphite is due to the layer-like structure, and the high melting-point is due to the strong forces in the layers.

It is generally thought that graphite is infusible, but according to Emeléus and Anderson [2] it can be melted and vaporised in a crucible made of sintered tantalum carbide, the latter having a melting-point of 3877° C.

Graphite is greatly superior to other carbonaceous matter, as it is less readily combustible, and so affords a better protection to the other materials used in the manufacture of the crucible.

Coke ground to powder is frequently used as a substitute for graphite in crucibles. It is not so satisfactory as the best graphite, being coarser and usually contains more ash, but is, nevertheless, extensively used.

Bricks made of compressed *gas coke* or *retort scurf*, or of a mixture of coke and tar, are occasionally used. They are described in Chapter VI.

Coal does not form a good substitute for coke or graphite, because it gasifies and burns away more rapidly than these materials. Its use is not to be recommended.

The value of any form of carbon for refractory work depends chiefly on its having a very low rate of combustion, and on its freedom from more than a small percentage of ash.

The carbides of various elements form an important class of refractory materials which are of special value in industries needing an extremely high temperature in association with strongly reducing conditions. They are too costly to use in the form of bricks, but are applied as a coating with excellent results. Crucibles and other small vessels of carborundum are too porous for use, and no means has yet been discovered for making them denser or for glazing them satisfactorily.

There are several different silicon carbides and carboxides sold under

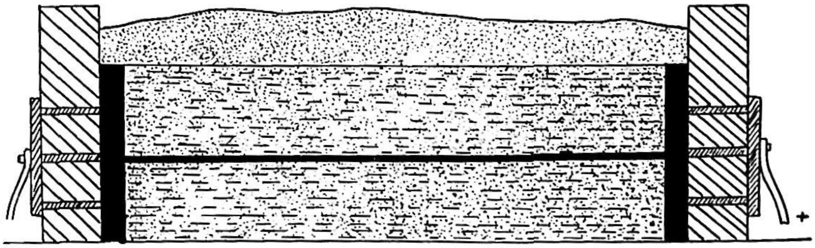

FIG. 31.—Carborundum furnace.

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[1] Bernal, *Proc. Roy. Soc.*, **A,** 1924, **106,** 749; Hassel and Mark, *Z. Phys.*, 1924, **25,** 317.
[2] *Modern Aspects of Inorganic Chemistry,* 1938, p. 451.

names such as *carborundum, crystolon, silfrax, silit, silundum,* and *siloxicon*; some of these are offered in several varieties and are merely different trade names for a more or less impure silicon carbide, but others are essentially distinct compounds, though the identity of some of these substances is by no means fully established. The distinction between carborundum and crystolon on the one part, and silundum and siloxicon on the other, is clearly recognisable, as the two former are composed wholly of carbon and silicon and appear to be true carbides, whilst the two latter contain oxygen and must be regarded as carboxides. The nature of silfrax, silit, and of several other similar products is not so well understood; they appear to be somewhat irregular mixtures of carbides and carboxides of silicon, together with some nitride.

All these materials are produced in an electric furnace by the partial fusion of a mixture of silica and carbon in the absence of air, and then cooling the material somewhat slowly so as to promote crystallisation. The furnace used (fig. 31) is usually about 33 feet long, 17 feet wide, and 10 feet deep, the only permanent part of the structure being the long end-walls and the floor. There is a large copper terminal head in each end-wall, and between them is a granular resistance core about 3 inches diameter, made of pieces of coke ⅝ inch diameter supported a short distance above the floor. This core is packed round loosely with a mixture of sand, coke, sawdust, and salt in proportions which depend on the nature of the product desired. An electric current of about 230 volts and 6000 ampéres is passed through the contents of the furnace, but after a time the current is increased and its voltage reduced until the heat is sufficient to clinker the contents of the furnace and convert them into carbides, etc. The temperature and rate of heating must be skilfully controlled in order that the desired product may be obtained, as the nature of the products varies with the proportions of the raw materials used and the conditions of heating and cooling. When the contents of the furnace are sufficiently cold, they are taken out carefully, each product being kept separate as far as possible. These products consist of some unaltered raw materials together with silicon carbide and various by-products of the reactions of which the more important are: (i) the graphitic core surrounded by (ii) a zone of crystallised carborundum, then (iii) a layer of carborundum powder, then (iv) a ring of siloxicon firesand (Si_2C_2O) with silicon monoxide, and (v) finally a film of silica.

The production of silicides and carbides by the reaction of carborundum on suitable metallic oxides has been patented (1906) by L. H. Baraduc and L. E. Müller as a material suitable for the manufacture of refractory bricks, but no particulars of their properties have yet been published. The use of a mixture of borax, alumina, and coke (which is said to form boron carbide and alundum) was patented in 1904 by J. Windholz.

Carborundum is a silicon carbide corresponding to the formula SiC; it is manufactured in an electric furnace as just described, but must be capable of formation at a much lower temperature, as it commonly occurs in plumbago crucibles which have been in use for some time. The usual charge is: sand 52 to 54 per cent., coke 35 per cent., sawdust 7 to 11 per cent., and salt 1½ to 4 per cent., these proportions being intended to be in agreement with the equation

$$SiO_2+3C=SiC+2CO,$$

but providing a slight excess of carbon. The function of the salt is to remove the iron and other impurities in the coke and sand by the formation of volatile chlorides. The sawdust is added to make the mass porous so that the CO may escape. The reaction takes place at a temperature between 1500° C. and 2200° C. (1820° C. to 1920° C. according to Lampen and Tucker, Gillet and Saunders).

Crude carborundum, freed from adherent matter by washing and treatment with sulphuric acid, contains about 65 per cent. of silicon, 30 per cent. of carbon, and 5 per cent. of impurities. It is in the form of hexagonal crystals varying in colour from the palest yellow to grey or blue-black, these variations being partly due to impurities in the material and partly to the play of light on the surface of the crystals. The crystals are of intense hardness, with a specific gravity between 3·17 and 3·21, and a melting-point of about 2500° C.[1] The refractoriness of carborundum is not known accurately, though the high temperature required for its manufacture shows that it can resist a much higher temperature than any firebricks now on the market. Unfortunately, it decomposes slowly at high temperatures (about 2250° C.) without fusing; the silicon volatilises and the graphite then burns away. The rate of decomposition is often reduced by the formation of siliceous glaze as one of the by-products, and this glaze is sufficiently protective to make carborundum valuable as a refractory material, especially for special work such as saggers, the tubular combustion chambers of Dressler kilns, and in parts of some other furnaces where it is not subject to much corrosion or to the influence of reducing gases. In the presence of flue- or kiln-gases, the decomposition of carborundum occurs more rapidly, carbon monoxide and silicon being formed. When ground to a powder and mixed with water, carborundum is entirely devoid of plasticity.

Carborundum differs from most refractory materials in its higher thermal conductivity, low coefficient of expansion, and its great strength and toughness. A comparison of some properties of carborundum with those of other refractory materials has been made by S. C. Linbarger, and is shown in Table XLIX.

TABLE XLIX.—PROPERTIES OF CARBORUNDUM, ETC.

Material.	Specific Heat.	Thermal Conductivity.	Compressive Strength. Lbs. per Sq. In.
Firebricks	0·192	0·0034	1,050
Sagger mixture	0·187	0·0033	1,340
Magnesite	0·220	0·0071	4,800
Chromite	0·174	0·0067	3,900
Refrax	0·162	0·0275	12,500
Carbofrax	0·180	0·0243	14,700
Silica	0·191	0·0020	2,300

Crystolon is the registered name for the carborundum made by one firm. It is produced by heating a mixture of sand, sawdust, and coke to a temperature of 1820° C. to 2250° C. At a temperature of 1600° C. a dark-coloured mass, known as amorphous silicon carbide or *firesand*, is formed, and this is converted slowly at 1850° C. into the crystalline crystolon. As the temperature approaches 2250° C., decomposition of the carbide occurs. Crystolon is not acted upon by acids, with the exception of hydrofluoric acid, but alkalies and alkaline carbonates readily decompose it when heated. Most metallic oxides react with it at a red heat. In an oxidising atmosphere, silicon carbide is decomposed, forming silica and carbon monoxide.

The coefficient of expansion of crystolon is 0·0000045 per 1° C.

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[1] Some samples show no signs of fusion at 2700° C.

Another form of silicon carbide is *silfrax*, which is produced by the action of the vapour of silicon on solid carbon; the surface of the latter being coated with small crystals of carborundum which are often tougher and stronger than larger carborundum crystals. As silfrax is formed at the same time as carborundum, each must be separated from the other when either is required in a fairly pure state. Silfrax is used for the manufacture of the same class of refractory articles as carborundum, the chief being pyrometer tubes and electrical fittings.

The highly crystalline carborundum is not usually employed as a refractory material, on account of the price charged for it, especially as the amorphous or crypto-crystalline carborundum, including that known as *firesand*, appears to be equally refractory. The minute crystals are much more stable than the amorphous material. For use as a refractory material, the powdered carborundum is mixed with 10 to 25 per cent. of its weight of refractory clays to secure a dense body of low porosity with about seven times the heat-conducting power of a sagger mixture and twelve times that of a silica brick, and a load-carrying capacity ten times as great as that of the ordinary sagger mixtures without the same tendency to soften at high temperatures. Hence, saggers made of carborundum need only be one-tenth of the present thickness, and are lighter and heated much more rapidly than the present ones. Articles made of carborundum will completely withstand sudden changes of temperature, and are not readily attacked by the fused ash from coal. At red heat, carborundum is attacked slowly by sodium carbonate, caustic soda, and sodium peroxide, and rapidly by red lead. It is not attacked by hydrofluoric acid to an appreciable extent.

By varying the conditions of manufacture, *siloxicon* and *silundum*—which consist of substances with the formulæ Si_2C_2O or Si_7C_2O, or of intermediate composition—are formed, provided the temperature of the furnace is not excessive.

Siloxicon was first isolated by Cohen in 1881, but was developed commercially and a method of manufacture patented by Acheson in 1903. Lampen and Tucker, Gillet and Saunders, have independently shown that it begins to form at a temperature of about 1500° C. Its composition varies, but is approximately Si_xC_xO, where $x=1-7$ and averages 2, but as hydrofluoric acid removes silica and silicon and leaves carborundum unattacked, siloxicon may be a solution of silica in silicon carbide. It is an amorphous substance usually possessing a greenish-grey sheen, and containing some free graphite and carborundum. It has a specific gravity of 2·52. It is highly refractory, a good electrical conductor, indifferent to most acids, but more easily oxidised at 1500° C. than carborundum, a superficial silica glaze being produced. When heated in a neutral or reducing atmosphere, it is unaffected until it reaches its decomposition temperature, about 1840° C., when it breaks down into carborundum, free silica, and carbon monoxide, or dissociates, forming carborundum and free oxygen.

According to Acheson, siloxicon has the advantage over carborundum of being a self-binding material, and, therefore, needs no bond when it is desired to mould it into bricks or other articles.

Fibrox (Eng. Pat. 16,299 of 1913) is a silicon oxycarbide prepared by heating a mixture of silicon and a catalytic agent such as fluorspar. Carbon monoxide and dioxide enter the crucible by diffusion and slowly convert the silica into a fibrous mass having a true specific gravity of 1·8 to 2·2. It is, however, extremely porous, 99 per cent. of the volume being air, and its apparent specific gravity is only 0·0025 to 0·0030. It is, therefore, excellent as a heat insulator.

Silundum is a term introduced in 1900 by F. Bolling of Frankfort, who found that when pieces of carbon, pressed or moulded to any desired shape, were heated in a mixture of silicon carbide and sand, the silicon reduced from the sand volatilised and combined with the carbon to form a compound which retained the shape of the latter.

Silundum is a compact form of silicon carbide with an excess of carbon. If silica is in excess, *silfrax* or *silit* is produced instead of silundum.

From a number of experiments made in 1914–15, Tucker and Lowry conclude that the formation of silundum commences above 1300° C., the greenish- or slate-coloured variety being first formed; whilst above 1800° C. the steel-grey modification appears. Above 2200° C. the product is decomposed and graphitic carbon remains behind. Both the green and the grey varieties of silundum are refractory; they are not attacked by oxygen, nitrogen, or hydrogen below 1100° C., nor by most fused salts; fused caustic alkalies and alkali carbonates convert the silicon into silica; they are oxidised by peroxides and by lead oxides; acids, even hydrofluoric acid, are without action on pure silundum, but attack the impurities present in the commercial products. The density is about 3, and the hardness 9 on Mohs' scale. The most notable distinction between the two varieties of silundum and carborundum is in their electrical resistance; the specific resistance per centimetre cube at 25° C. of carborundum is 50 ohms; that of green silundum is 0·2374 ohm; at higher temperatures all these carbides become fairly good conductors.

Tucker and Lowry consider that the green silundum is a silicon carboxide with about 9 per cent. of oxygen, and closely resembling siloxicon. It decomposes at a higher temperature, forming the grey variety of silundum, which appears to be a carbide closely resembling carborundum in composition, and devoid of oxygen. It is very important that all carbides used as refractory materials should be as devoid as possible of free carbon; this material, even when present in only small amounts, is a serious hindrance to that intimate contact between the bond and aggregate which is essential to the production of sound goods.

All the carbides, nitrides, and borides may be obtained by heating the powdered metal with carbon, boron, or nitrogen in a stream of nitrogen at 2200° C. for the carbides, 1800°–2000° C. for the borides, and 1100°–1200° C. for the nitrides. The products may be purified by heating them—in the form of compressed rods—in an inert atmosphere at 2500° C. or above, when all impurities are volatilised.

// *Properties.*—The properties of the various forms of silicon carbide of chief interest in the refractory materials industry are their high thermal and electrical conductivities, great mechanical strength when hot and resistance to abrasion, as well as their hardness and refractoriness. Silicon carbide is devoid of plasticity, and so must be bonded with clay or other binding agent. It is highly resistant to acids and alkalies. Silicon carbide is well suited for use in muffles and other parts of furnaces where a high thermal conductivity is advantageous. It will not withstand basic slags or molten metal. The specific heat varies with the source from 0·150 to 0·186. Its electrical conductivity is about 0·024; its thermal expansion from 200° to 900° C. is 0·0000047; its specific gravity is 3·1 to 3·3, and its porosity (water absorption) 15–20 per cent. (by weight). On prolonged exposure to air at 1500° C. it decomposes slowly, the carbon burns away, and the silicon is converted into silica; if the temperature is sufficiently high the silica may fuse and form a protective coating over the rest of the material.

The carbides have much in common with true metals, including high electrical and thermal conductivities and some paramagnetic properties. Most carbides are also very hard, and highly refractory.

Tantalum carbide is resistant to nitrogen, but other carbides tend to form nitrides.

Zirconium carbide, ZrC, is formed by heating zirconia with carbon at 1700°–2000° C. It is highly refractory and very inert, but is slowly decomposed by oxidising agents. It appears to be worth attention as a refractory material.

Titanium carbide, TiC, is made by heating titanous oxide with carbon at 1700°–2000° C. It crystallises readily and melts at $3410 \pm 90°$ C. It burns slowly in oxygen at a red heat, but is worth attention as a refractory material.

Boron carbide is also highly refractory. Three boron carbides are known; the most important is B_4C, obtained by the direct combination of boron and carbon (boric acid and coke) in the electric furnace. It is a black crystalline substance of great hardness; melting-point about 2350° C. It is neither decomposed nor volatilised below 2800° C. It is attacked by oxygen and by chlorine at 1000° C. and above.

Complex carbides are used; *e.g.* Siemens and Halske A. G., in 1932,[1] patented the use of a preformed hard carbide of boron, titanium, silicon, zirconium, cerium, thorium, or any two or more of these carbides.

Nitrides.—Various metallic and other nitrides are made in a similar manner to silicon carbide, but the materials must be heated in a current of nitrogen. The nitrides, particularly *boron nitride, tungsten nitride,* and *molybdenum nitride,* have similar properties to the carbides, but are more resistant to acids and alkalies.

Boron nitride is formed when boron in heated to 1250° C. in an atmosphere of nitrogen. It may also be prepared, according to E. Podszus, by heating boric oxide in an atmosphere of anhydrous ammonia gas under a high pressure at a temperature of 1200° C. The ammonia is decomposed, the nitrogen combining with the boron to form boron nitride. It is a white, amorphous, and soft material, similar to talc, and is infusible at the melting-point of tungsten. It can readily be compressed wet or dry into rigid articles, and for use at very high temperatures it is one of the best insulators known. It has a reducing action on many metallic compounds, but zinc and iron do not affect it. It is also attacked by potash compounds. It cannot be used in an oxidising atmosphere or in association with boiling water or steam, as it is readily attacked by these substances.

Boron nitride has been recommended by E. Podszus [2] for tubes for electric furnaces on account of its low thermal conductivity. Schwarz has used powdered boron nitride as a packing between the tubes in an electric furnace.

The use of *aluminium nitride* for bricks was patented in 1912 (Eng. Pat. 1961) and in 1921 (Eng. Pat. 189,781).

The *nitrides,* whilst highly resistant to heat, are of small commercial value for refractory purposes, as they are decomposed so readily by moisture, especially if carbon dioxide is present. Small proportions of various nitrides are often present in commercial carbides; they are seldom of importance and may generally be neglected.

Borides.—Various metallic borides are highly refractory. They are made by heating the powdered metal with boron *in vacuo* to 1800°–2000° C. The best-known borides are zirconium boride and tungsten boride. The borides are intensely hard, highly refractory, and resistant to acids and alkalies. At very high temperatures they are attacked by air and other gases.

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[1] Eng. Pat. 422,961.

[2] *Zeits. f. angew. Chem.*, 1917, **30**, 153.

The following table[1] shows the approximate melting-points of various carbides, nitrides, and borides:—

TABLE L.—MELTING-POINTS AND HARDNESS VALUES OF CARBIDES, NITRIDES, AND BORIDES.

	Formula.	Melting-point, ° C.	Hardness (Mohs').
Carbides.			
Molybdenum carbide	Mo_2C	2687	..
,, ,,	MoC	2677	..
Hafnium ,,	HfC	3887	..
Tantalum ,,	TaC	3877	..
Titanium ,,	TiC	3137	8–9
Tungsten ,,	W_2C	2957	9–10
,, ,,	WC	2857	..
Zirconium ,,	ZrC	3532	8–9
Nitrides.			
Tantalum nitride	TaN	2087	8–9
Titanium ,,	TiN	2947	8–9
Zirconium ,,	ZrN	2982	8
Borides.			
Tungsten boride	WB	2882	8
Hafnium ,,	HfB	3062	..
Zirconium ,,	ZrB	2992	9

A mixture of 80 per cent. of tantalum carbide with 20 per cent. of zirconium carbide melts at 3942° C.—the highest melting-point of any known substance.

The carbides and nitrides may be purified (in small quantities) by heating to just below the melting-point, at which temperature almost all the impurities are volatile.

The crystal structure[2] of the refractory metallic carbides may be compared to a mass of relatively large spheres of metal with the (much smaller) carbon atoms filling the interstices and causing only a small expansion of the crystal-lattice. The composition is determined by the number of geometrically equivalent positions between the close-packed metal atoms. The tendency to form 1 : 1 compounds, irrespective of the valency of the components, is noteworthy. The typically salt-like carbides of the strongly electro-positive metals (Al_4C_3, Be_2C, CaC_2, Mg_2C_3) have a very different structure, analogous to hydrocarbons stripped of their hydrogen atoms and inserted interstitially in the metal crystal-lattice.

Chromite, or chrome iron ore, is a double oxide of iron and chromium. It occurs almost entirely in basic igneous rocks such as peridotites, dunite, pyroxenite, etc., and in residual clays. Much of the chromite occurring in igneous rocks is of little commercial value, as it is disseminated through the rock. Only the segregated material is worth development.

The massive chromite in residual clays is at present most largely used, and supplies the greater portion of the world's demand.

It is chiefly obtained from North America, Norway, South Africa, New Caledonia, Russia, Greece, Turkey, Southern Rhodesia, and elsewhere.

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[1] J. S. Anderson, *Chem. Ind.*, 1937, **56**, 766; and other sources.

[2] J. S. Anderson, *Chem. Ind.*, 1937, **56**, 767.

The American deposits have greatly increased in importance during the last few years, chromite being now obtainable from Quebec, California, Oregon, Wyoming, and Alaska in large quantities. In Quebec (Canada), chromite occurs in association with serpentine rocks. The chromite in this locality varies considerably in quality, ranging from 20 to 50 per cent. of chromic oxide. Considerable quantities have also been obtained during the last few years from the northern part of Cuba.

The extensive deposits in the Orange Free State have not, up to the present, been developed owing to the comparatively small demand for the ore. The Bhodesian deposits are chiefly in the form of lenticular masses associated with talc schist and serpentine. The chromite is mined extensively in the South of Rhodesia around Selukwe, where some of the lenses are of large size and contain 42 to 51 per cent. of chromic oxide. Chromite also occurs along the edge of the Bushveld granitic area in the Transvaal, the ore containing 35 to 45 per cent. of chromic oxide, whilst a thick band of chrome ore also occurs in the Lydenburg district.

The principal deposits of chromite in India are found in the Protectorate of Baluchistan as veins and segregated masses in association with serpentine and igneous intrusions of Upper Cretaceous age. The deposit is, in some places, very pure, and at Khanozai contains 54 per cent. of chromic oxide. A lower grade of chromite also occurs as a vein in serpentine in Mysore. The material in some places contains 52 per cent. of chromic oxide, but the average chromium content is much lower. Ore of good quality is also obtained in the Singhbhum district.

In New Caledonia, chrome ore occurs in association with serpentine and ferruginous clay, that in association with the latter being of a high grade and readily obtainable. This deposit supplies the bulk of the chromite used at the present time.

The Brusa district of Asia Minor yields a chrome ore of good quality containing about 50 per cent. of chromic oxide. Other deposits in Asia Minor occur at Miram, Kosludja, Artranlar, and Kaliar; they have been worked considerably.

Chromite is obtained in small quantities in the island of Uist and in the Shetland Islands, where it is associated with serpentine rocks. The Hagdale Quarry contains very large masses of good quality ore, though in other districts the quality varies considerably.

Chromite occurs in the eastern provinces of Greece and in the island of Skyros, also at Gorantza, Grechane, and Uskub in Serbia, at Queimadus, Santa Luzia, and Bom-Fim in Brazil, and in the Jalapa district of Guatemala, the Brazilian deposits being of the greatest importance.

A placer deposit of chromite sand is worked in Oregon, U.S.A., the ore being separated magnetically. In most cases, chromite deposits are very uncertain and irregular; some of the pockets are very large, whilst others are promising at first but fail suddenly.

Chromite is obtained both by mining and quarrying according to the nature and size of the deposit. The crude ore is then picked by hand and, if necessary, ground and concentrated mechanically. The chromite in Quebec was first passed through a jaw crusher and then reduced to a powder in a stamp mill, so that it all passed through a No. 20-mesh sieve; the ground material was then concentrated on Wilfley tables. A similar method is still employed at Brusa in Asia Minor. It is specially necessary to clean the ore from the associated serpentine, which makes it very fusible.

Finely ground chrome iron ore can be purified by elutriation, as most of the impurities are of much lower specific gravity.

Properties.—Pure chromite corresponds to the formula $FeO.Cr_2O_3$,[1] which represents 68 per cent. of chromium oxide and 32 per cent. of ferrous oxide, but ores containing 60 per cent. of chromium oxide are rare and many contain less than 35 per cent.; the latter should not be used for chromite bricks. This variation in composition is partly due to the fact that in chrome ore having the general formula $XO.Y_2O_3$, X can represent Fe, Mg, or Ca, and Y Cr, Al, or Fe. It is found that chromites from different sources behave so differently (*e.g.* as regards constituents soluble in hydrochloric acid) that they appear to be differently composed. At present there appears to be no pure chromite, but a chromite-complex in which some of the constituents are not combined in the ordinary manner, but in some looser form of compound. In this connection Seil[2] has shown that most chrome ores consist of two parts: (i) a complex spinel of the type $(Fe,Mg)O.(Cr,Al)_2O_3$, comprising 75–90 per cent. of the whole; and (ii) a magnesium silicate bond.

The chief impurities are olivine, talc, chlorite, serpentine, and free silica. Chrome ore containing more than 8 per cent. of silica is not satisfactory for chromite bricks. The microscope and X-ray spectra are the best 'tests.'

The specific gravity of chromite is about 4·5. The chief value of chromite lies in its neutrality, *i.e.* in its being highly resistant to slags, silica, and magnesia.

The purest ore melts at 2180° C., but commercial ore has a refractoriness between 1700° and 1900° C. That with a refractoriness less than Seger Cone 35 should not be used for chromite bricks. The refractoriness alone is not a reliable guide, as chrome iron ore softens well below its melting-point, and the refractoriness under a load of 28 lbs. per sq. in. is only 1330°–1380° C.

There seems to be some relation between the silica-content and the refractoriness, a small proportion of silica greatly reducing the heat-resistance. It is, therefore, important to insist on a high refractoriness. The most fusible mixture of chromite and clay contains 64 per cent. of chromite and melts at 1460° C.[3]

A fused mixture of the oxides of chromium, aluminium, silicon, and magnesium is stated in Eng. Pat. 324,312 to be highly refractory; similar, but less complex, mixtures are the subject of Eng. Pats. 360,572, 382,014, 409,130, 435,448, 441,516, 451,493, 456,207.

The chief oxides which reduce the refractoriness of chrome ore are: silica, ferric oxide, alumina and magnesia.

TABLE LI.—TYPICAL ANALYSES OF CHROMITE.

<table>
<tr><th>District.</th><th>Chromic Oxide.</th><th>Lime.</th><th>Magnesia.</th><th>Iron Oxide.</th><th>Alumina.</th><th>Silica.</th></tr>
<tr><td>Rhodesia</td><td>42–51</td><td>..</td><td>8·5–15·0</td><td>18·5</td><td>14·5–16·5</td><td>4·5</td></tr>
<tr><td>New Caledonia</td><td>54·5</td><td>1·5</td><td>8·0</td><td>17·5</td><td>11·0</td><td>3·0</td></tr>
<tr><td>Turkey</td><td>51·7</td><td>1·7</td><td>14·3</td><td>14·2</td><td>14·1</td><td>3·5</td></tr>
<tr><td>Bosnia</td><td>50·5</td><td>some</td><td>some</td><td colspan="2">39–45</td><td>2·5</td></tr>
<tr><td>Quebec</td><td>50·5</td><td>2·0</td><td>16·0</td><td>18·0</td><td>10·0</td><td>3·0</td></tr>
<tr><td>Mysore</td><td>51·0</td><td>0·5</td><td>12·0</td><td>22·5</td><td>7·5</td><td>4·5</td></tr>
<tr><td>Baluchistan</td><td>56·0</td><td>1·0</td><td>15·0</td><td>13·0</td><td>11·0</td><td>1·0</td></tr>
</table>

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[1] In considering analyses of chromite it must be remembered that most of the iron is present in the ferrous state as $FeO.Cr_2O_3$, and not as ferric oxide as usually reported.

[2] *Bull. Penn. State Coll. Mineral and Exptl. Sta.*, 1934, **14**, 40.

[3] *Trans. Amer. Inst. Min. Eng.*, 1918, **59**, 154.

M. Simonis has recently determined the melting-point of mixtures of chromite and Zettlitz kaolin. The chromite was composed of chromic oxide 52·9 per cent., ferrous oxide 22·6 per cent., alumina 4·8 per cent., magnesia 10·1 per cent., and silica 9·6 per cent. His investigations showed that as the percentage of chromite increased from 0 to 30, the melting-point fell rapidly from Seger Cone 35 to Cone 17, then less rapidly to Cone 15 at 65 per cent. (the eutectic-point). It then rose rapidly, reaching Seger Cone 35 again at 80 per cent., Cone 41 at 90 per cent., and higher undetermined temperatures with greater percentages of chromite. Chromite can, therefore, be mixed with as much as 10 to 15 per cent. of kaolin for plasticity and still yield a highly refractory mass.

In addition to its use as a brickmaking material, chromite is largely employed for patching open-hearth furnaces.

Chrome spinels are compounds of chromite and magnesia having the general formula $RO.Cr_2O_3$. They are practically infusible and have been used fairly extensively for highly refractory bricks for steel-making furnaces. For this purpose artificial spinels made by mixing magnesia and chromite are generally used (see " Chrome Spinel Bricks ").

For chrome spinel bricks the chrome ore should be low in silica; if possible there should be less than 5 per cent. and in any case less than 8 per cent. The best bricks contain magnesia and chromite in the ratio 1 : 3 with all the magnesia in the finest portion, but as an indication of the wide variations possible it should be noted that one make of chrome-magnesia brick well known in the English market consists of—

	Per cent.
Magnesia	39
Chromic oxide	24
Alumina	16
Ferric oxide	14
Silica	5

BASIC REFRACTORY MATERIALS.

The chief refractory materials of a basic character are—

1. *Alumina.*[1]
2. *Iron ores.*
3. *Lime.*
4. *Magnesia.*
5. *Dolomite* (magnesian limestone).
6. *Rarer oxides,* particularly *zirconia.*

Alumina is the oxide of the metal aluminium. It occurs in nature in a crystalline form as *corundum* and as *emery,* the latter being far from pure and almost useless as a refractory material. Hydrated alumina occurs in such forms as *bauxite, laterite, diaspore, hydrargillite* or *gibbsite, cliachite, shanyavskite, alumogel,* etc.; the latter are probably of colloidal origin. The only crystalline forms are diaspore and hydrargillite, and these may be derived

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[1] Alumina behaves as a neutral substance, a constituent of an acid, or a base, according to the conditions under which it is used. Its inclusion here among the basic materials is, therefore, mainly as a matter of convenience.

from colloidal forms by subsequent crystallisation. Bauxite and laterite are of very variable composition, and are probably mixtures of other forms of hydrated alumina. The best specimens of bauxite do not contain more than 90 per cent. of alumina.

Pure crystalline alumina is lustrous and vitreous ; it has a specific gravity of 3·9 and a hardness of 9 on Mohs' scale. The natural mineral (corundum) is of small importance, but artificially prepared corundum is of great commercial value.

The properties of precipitated alumina are quite different from those of crystalline alumina and more closely resemble those of bauxite. Thus, precipitated alumina is soluble in mineral acids, but after heating to 850° C. or above it becomes insoluble.

According to O. Ruff and O. Goecke, alumina heated in nitrogen at ordinary atmospheric pressure melts at 2020° C., but it vitrifies considerably at 2009° C. As would be expected, the temperature remains constant so long as the melting continues. No volatilisation was observed, so that the boiling-point of alumina must lie considerably above 2020° C.

Under reduced pressure, volatilisation of alumina is observable at 1690° C., and is very marked at 1740° C., with a pressure in the furnace of only 6 mm. of mercury. The volatilised and re-deposited alumina melts at 2035° C.

Diaspore ($Al_2O_3.H_2O$) occurs in the form of orthorhombic prismatic crystals and also as white foliated and scaly forms, with a hardness of nearly 7 and a specific gravity of 3·5. Recently, it has been used in the United States as a refractory material, and it is regarded as superior to bauxite on account of its lesser contraction due to the smaller amount of water it contains.

Laterites are seldom suitable for use as refractory materials, but the purer varieties may be so employed. They appear to be derived from basaltic or doleritic rocks by the action of alkaline waters, or possibly by bacteria. The manner in which this action takes place is not known, though it has been suggested that lateritisation is due to conditions, very imperfectly understood, in which ordinary clays are partially decomposed into free alumina and free silica, and form laterites. The action occurs particularly in tropical regions, one of the best-known developments of fairly pure laterite being in the basaltic plateau region of the Deccan in India. The enormous deposits of laterite in China are much too impure for refractory purposes.

Usually, laterite is a reddish, somewhat cellular, clayey material with ferruginous concretions, and it hardens considerably on exposure to the air. It consists largely of hydrated oxides of aluminium and iron with a variable percentage of silica ; some varieties with little silica approach bauxite very closely in composition.

Bauxite derives its name from the hill *Colline les Baux* near Arles in South France. Its use for bricks was first suggested by Gaudin in 1858.

Bauxite occurs extensively—

In *Ireland* in Antrim, as thin seams between sheets of basalt, from which it is thought to have been formed by weathering. Some of the seams are 3 to 7 feet thick. Bauxite is associated, in different places, with lithomarge and lignite ; near Straid it is replaced by a pisolitic iron ore.

In *Australia* at Winyello, south of Sydney.

In *France* at Hérault, Var, Charente, Valle Verac, and in many localities along the Mediterranean and in the East Pyrenees. It occurs chiefly in irregular or globular masses in pockets in the limestone of these districts. Bauxite also occurs as a decomposition product of gneiss and basalt at Puy-de-Dôme.

In *Germany* in Steiermark, Hesse, Offenbach, and Giessen.

In what was *Czecho-Slovakia* in North-east Carinthia and Torda-Aranyos.

In *Italy* in Calabria, intercalated with chalk.

In *Africa*, the deposits containing iron in varying proportions. Extensive beds of better quality occur on the Gold Coast in the Kwabu district.

In *India* in the Balaghat and Jubbulpore districts in the Central Provinces. In *Russia* the bauxite is of poor quality.

In the *United States* in Georgia, Arkansas, North Carolina, and Alabama. The principal deposits are in Arkansas, where some of the deposits are 30 feet thick. They are overlain by sands, gravel, and clay, and rest upon decomposed syenite. In Georgia, the deposits are associated with Cretaceous and Tertiary clays and sands, and in Tennessee they occur in limestone-dolomite-chert rocks.

In *South America*, the deposits are of good quality and contain only small quantities of iron and titanic oxides and silica. A deposit on the banks of the Demerara River in British Guiana contains 67 per cent. of alumina.

In *Rumania*, especially in the Bihar Mountains, where the bauxite occurs in association with Jurassic limestones. The deposits contain 20 to 30 per cent. of iron oxide and 50 to 60 per cent. of alumina, small quantities of titanic oxide and silica also being present.

Deposits of bauxite also occur in Dalmatia and in Herzegovina; these were used largely during the war for supplying Germany and Austria.

The best qualities of bauxite occur in the South of France, North America, and in India. The Irish bauxite is much richer in iron oxide.

In chemical composition, bauxite may be regarded as an impure aluminium hydroxide, the origin and nature of which is by no means clearly known, though it is generally thought to be derived from the decomposition of basaltic or doleritic rocks, possibly by a process of laterisation.

It is exceedingly difficult to ascertain the manner in which bauxite is produced in nature; its surroundings offer but little information, as it occurs sometimes in basalt, sometimes in limestone, and sometimes in sandy clays.

A true bauxite has a specific gravity of about 2·9 and is rather softer than gypsum, though some concretionary masses may have a hardness corresponding to 6 on Mohs' scale. Theoretically, it should not contain any silica, though some is always present in natural bauxites.

The composition of bauxite varies greatly, but that of the best specimens of raw (unburned) bauxite varies between the following limits:—

Alumina	50 to 90 per cent.
Silica	3 ,, 25 ,,
Iron oxide	½ ,, 12 ,,
Water	10 ,, 30 ,,

Titanic oxide, manganese oxide, vanadic oxide, lime, magnesia, alkalies, sulphuric acid, phosphoric acid, etc., in small quantities, seldom exceeding a total of 8 per cent.

In North Ayrshire, Scotland, a thick bed of bauxitic fireclay from 6 to 24 feet thick occurs in the Millstone Grit series, immediately above several lava flows containing beds of foul coal, fireclay, and ganister. This material appears to be a very compact, partially silicified bauxite, with a conchoidal fracture, oolitic structure, and a high percentage of alumina, but it differs from true bauxite in that only about 16 per cent. of the alumina appears to be in the free state, the remainder being combined with silica to form a mineral resembling kaolin. Moreover, the free alumina is not so soluble in acids as that in true bauxites. Its refractoriness is greater than that of Cone 35. A similar material in the Kilmarnock district is not so refractory as that of the same bed in the west.

The essential constituent of bauxite does not appear to consist of the same substance in all cases, as it possesses marked colloidal properties and appears to be very largely composed of hydrogels in a partially dehydrated state; this accounts for its variable content of "combined water" and for the great shrinkage which it undergoes when heated. R. Wholin has found that—

(i) Some samples lose 12 to 14 per cent. of combined water at 540° C., and appear to correspond to $Al_2O_3.H_2O$ (diaspore).

(ii) Some samples lose 27 to 35 per cent. of water at about 310° C., and correspond to hydrargillite, $Al_2O_3.3H_2O$.

(iii) Other samples appear to be mixtures of the two foregoing, and lose water at two distinct temperatures.

(iv) Siliceous bauxites have a heating curve which indicates that they contain a considerable proportion of clay.

Lienau has classified the different bauxites as follows:—

1. Bauxites of the type $Al_2O_3.H_2O$, corresponding to diaspore. This type occurs chiefly in South France, particularly near Var and Hérault. Average loss on ignition 12 to 14 per cent.

2. Bauxites of the type $Al_2O_3.2H_2O$, or true bauxite. They occur chiefly in Les Baux. Average loss on ignition 20 to 24 per cent.

3. Bauxites of the type $Al_2O_3.3H_2O$, with a loss on ignition of 27 to 35 per cent., corresponding to hydrargillite.

Dittler and Doelter prefer a physical classification to a chemical one, and divide the bauxites into—

(*a*) True bauxites, derived from colloidal and non-plastic materials.

(*b*) Mixtures of colloidal and crystalloidal alumina, containing but little of the colloid and much hydrated iron oxide. This group has probably been derived from impure crystalline hydrated alumina.

(*c*) Plastic bauxites, largely derived from ferruginous clays.

Commercially, bauxites are divided into three groups, according to their colour—

Red bauxite has a brick-red colour, and is commonly regarded as a mixture of purer bauxite with iron oxide, though many of its characteristics do not indicate such a mixture, but rather a separate compound. For most purposes, where a refractory material is required, the red bauxite is too fusible, and the cost of purifying it (which may involve the use of an electric furnace) is too high for all except small articles, such as crucibles used for special investigations.

The red bauxite of the Var is noted for its low proportion of silica, which is under 1 per cent.

White or *grey bauxite* sometimes has a yellowish tinge. It is essentially an alumina compound, though often containing large proportions of silica, water, etc., as described in the foregoing pages. When bauxite is specified for refractory work, a good quality of white bauxite is to be understood, and in the following pages it is the white bauxite which is intended. It is a curious fact that the red bauxites are often richer in alumina than the white variety, notwithstanding the iron in the former. The statement is sometimes made that white bauxites are akin to the china clays or kaolins; this is not the case, the two materials having nothing in common except their refractoriness, and occasionally an accidental resemblance in the figures which each gives on analysis.

Blue bauxite owes its colour to the colloidal ferrous sulphide which it contains.

For refractory purposes, those bauxites are the best which contain the largest proportion of alumina with the smallest proportion of silica, iron, titanic, and other fusible oxides. The proportion of silica is not often of great importance, though experience seems to show that the best bauxite bricks contain equal molecules of silica and alumina, *i.e.* a silica : alumina ratio of 1 : 1·7, but some bauxite bricks with a ratio of 1 : 3·5 have proved highly satisfactory. The presence of more than 5 per cent. of titanic oxide or of more than 10 per cent. of iron oxide is highly objectionable for bauxites to be used for refractory purposes.

The effect of heat on bauxite resembles that on the purer clays, as will be seen on comparing fig. 32 with figs. 20 to 22. Bauxites of different origins behave differently: thus, in fig. 32, **1** is a nearly pure diaspore ($Al_2O_3.H_2O$); **2** is a Hungarian bauxite containing 58 per cent. of alumina and 23 per cent. of iron oxide; **3** is a French bauxite from Cettes, containing 56 per cent. of alumina and 25 per cent. of silica; **4** is another French bauxite from Villevoyrac, containing 62 per cent. of alumina and 20 per cent. of silica; **5** is from St Chanien in South France, and is similar to **4** in composition.

Although it is impossible at the present time to separate these bauxites into different minerals, there is reason to suppose that those yielding curves **3, 4,** and **5** in fig. 32 are mixtures of clay and true bauxite, whilst **1** and **2** are curves of diaspore, even though **2** may be sold commercially as bauxite.

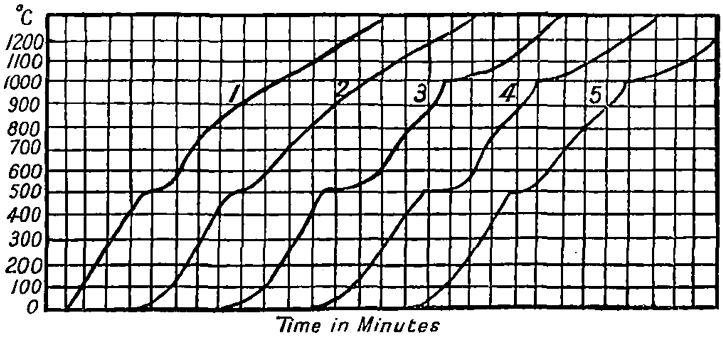

FIG. 32.—Thermal curves of bauxite. (*R. Rieke.*)

The thermal curve obtained when mixtures of bauxite and china clay are examined is similar to curves **3, 4,** and **5,** and has the two characteristic points at 500° C. and 1060° C. respectively. From this and other observations, R. Rieke concludes that the true bauxites only show the lower characteristic in the curves (as **1** and **2**), and that those which show the exothermic reaction at the higher temperature are mixtures of bauxite and clay. Bauxite clays have a mean coefficient of expansion of 0·61 per cent. from 0° C. to 1000° C.

Houldsworth and Cobb [1] found that Irish red bauxite showed an endothermal reaction between 490° C. and 565° C., and an exothermal reaction at 1000° C. to 1070° C., whilst grey bauxite showed three endothermal reactions: (*a*) up to 180° C., (*b*) 300° C. to 365° C., and (*c*) 510° C. to 620° C., and an exothermal reaction between 940° C. and 965° C. The latter result confirms those of Bigot, who found that bauxites containing more than 14 per cent. of water lost it in two stages, viz., at 300° C. and 500° C. respectively, whilst those with less than 14 per cent. of water lost it almost entirely above 500° C.

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[1] *Trans. Eng. Cer. Soc.*, 1922–1923, **22** (ii), 111.

It will be observed that natural bauxites lose all their combined water at temperatures below 600° C., and that calcining at higher temperatures is unnecessary as far as the removal of this water is concerned. In practice, however, the decomposition of the bauxite is so slow at temperatures below 1200° C., that this temperature is usually attained in calcining bauxite on a commercial scale. The higher temperature causes the bauxite to shrink, possibly as a result of polymerisation.

Alumina, prepared artificially, behaves differently from natural bauxite, and may not show the same curves. Precipitated aluminium hydrate which has been heated to 100° C., so as to form alumina, contains no combined water, and, therefore, does not show any critical range comparable to those in natural bauxites.

Houldsworth and Cobb[1] found that alumina, prepared by calcining aluminium nitrate, showed only an exothermal reaction between 1060° C. and 1130° C.—due possibly to the polymerisation of alumina, which confirms Whölin's figure. Mellor gives a lower temperature, viz.: Precipitated alumina, after air-drying, showed endothermic reactions at 70° C. to 155° C., and 365° C. to 480° C., but no exothermic change at 1060° C., the changes at the two lower temperatures being possibly connected with the dehydration of the alumina.

The value of bauxite (which depends on the proportion of alumina it contains) is seriously diminished by even a small increase in the proportion of other oxides. The unburned material often contains as much as 30 per cent. of water, so that in comparing the results of analyses of different samples, the calculation should be made on the calcined samples.

Bauxite may be improved by washing in a continuous stream of water flowing at such a speed as to remove some of the free silica. It may also be treated advantageously in a separating machine, in which the powdered material is subjected to the action of a stream of water in a rapidly revolving drum. This effects a very good separation of all the coarser impurities and much of the fine siliceous matter.

Raw bauxite is completely soluble in hydrochloric or sulphuric acid, but on prolonged ignition it becomes insoluble. Its specific gravity is about 2·55, but increases with the temperature if the bauxite is heated.

Bauxite must be calcined before use owing to the excessive contraction of the raw material on heating. When used for brickmaking, it is usually mixed with about one-fourth its weight of clay, ground, tempered slightly with water, formed into rough bricks, and burned.[2] Care should be taken that it is not "flashed" by the flame of the kiln, as pieces discoloured in this way by the reduction of the iron present will cause trouble when the material is ground up with more clay for use. For this reason, so-called bauxite bricks usually contain nearly half their weight of clay. On the other hand, bauxite may be used satisfactorily in the place of grog for increasing the refractoriness of fireclays, as, being composed almost entirely of alumina, it to a large extent neutralises the combined effect of silica and fluxes, and enables bricks of best quality to be made from inferior clay, though its value for this purpose can be overestimated. Bauxite cannot be used alone for the manufacture of bricks on account of its lack of plasticity, but when added to clay it reduces the contraction, both in drying and firing, and increases its resistance to high temperatures. When purchased for rendering clay more refractory, the presence of over 12 per cent. of iron oxide in the bauxite is objectionable.

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[1] *Trans. Eng. Cer. Soc.*, 1922–1923, **22** (ii), 111.

[2] The raw bauxite cannot be used, as it shrinks excessively on heating.

The proportion in which bauxite is to be mixed with the ordinary fireclay of the works varies according to the nature of the goods to be made, but one part of fireclay is frequently used to each four parts of bauxite—more bauxite being used in the case of very large articles.

Bauxite is occasionally used without any admixture of clay, but lime-water must, in this case, be employed in the tempering, and the bricks prepared in much the same manner as Dinas bricks.

Provided that pure materials are used, there is a large field for further work in this direction, the chief difficulties being the shrinkage and high cost of the bauxite, and the shortness it gives to clays mixed with it, on account of its non-plastic quality. It has been found to stand particularly well for the linings of rotary puddling furnaces and for other furnace linings where great refractoriness is required apart from great mechanical strength. Under long-continued heating at 1400° C., bauxite changes into a substance as hard and infusible as natural emery.

The successful employment of bauxite requires some amount of skill and experience, as too much and too little bauxite are equally improper; the proportion used must depend on the composition and general nature of the clay it is desired to make more refractory.

Bauxite may be purified and pure alumina obtained by roasting the crude material so as to oxidise the iron, fusing the roasted material with caustic soda or sodium carbonate and treating the cold mass with water. The alumina is then precipitated by agitation with a small quantity of aluminium hydrate or by passing carbon dioxide through the solution. The precipitate may then be washed, dried, and ignited, when the product is almost pure alumina.

With some bauxite the preliminary roasting is not necessary; in that case the dried and pulverised bauxite is heated with a strong solution of caustic soda under pressure at 150° C. The insoluble impurities are separated and the alumina precipitated by adding a little aluminium hydroxide and stirring. The precipitated alumina is afterwards washed, dried, and calcined at about 1100° C.

The pure calcined alumina made in this way melts at 2000° C. to 2050° C., according to its purity. Though devoid of plasticity, it is easily mixed with clays, and forms the most valuable material yet discovered for increasing the refractoriness of a relatively pure clay to the highest possible extent. It has all the advantages of bauxite, with few of its drawbacks, and is unquestionably the best material to use when cost is a minor consideration.

Gibbsite or *hydrargillite*, Al(OH)$_3$, is chiefly of academic interest as it is one of the minerals occurring in some clays. It occurs in massive form in Dutch Guiana, South America, and in Georgia, U.S.A. The purest gibbsite occurs in the form of egg-shaped nodules embedded in a softer and less pure matrix.

Gibbsite usually contains little impurity (chiefly 1–5 per cent. of silica and 1–4 per cent. of titanium dioxide), but some samples contain 16 per cent. of silica.

When pure, gibbsite melts at 2035° C., but the commercial material melts at 1850°–2025° C. The specific gravity is 2·4. The shrinkage on heating is similar to that of highly plastic clays. *Gibbsite,* on heating, forms *boehmite,* and this, in turn, another form of alumina with a spinel-like structure. The crystal unit of gibbsite consists of two hydroxyl sheets in each layer of the lattice approximately in closest packing, with four aluminium ions between six hydroxyl groups above and six below (making twelve hydroxyl groups in all), but only two-thirds of the possible positions are occupied. Each

OH of one layer is opposite an OH of the next layer, as if there were a strong attraction between them. The crystals are monoclinic; $a=8{\cdot}624$, $b=8{\cdot}060$, $c=9{\cdot}699$, $\beta=85°\ 26'$. The formula for the unit cell is $Al_4O_{12}H_{12}$.

All natural forms of alumina, except corundum, shrink continuously up to their melting-point and should, therefore, be calcined at as high a temperature as practicable before being used. Pure alumina after being heated to 1900° C. is quite impermeable.[1] Articles made of it can be used up to a temperature of 1950° C.

Sintered alumina is made by heating commercially pure alumina to incipient fusion or vitrification, but not sufficiently to convert it into a fluid. *Sintercorund*[2] is a trade-name, though often used for sintered alumina (see p. 210).

Fused alumina is best obtained from the purest commercial " hydrate of alumina "; but as this is commonly regarded as too costly, bauxite is frequently employed. The bauxite[3] is first calcined to remove all the " combined water "—a temperature approaching 1200° C. being required for this purpose when working on a large scale, though under suitable conditions the whole of the water can be driven off at 700° C. The calcined alumina is then heated in an electric furnace until it is fused; after a sufficient quantity has been obtained the furnace is allowed to cool slowly and the charge is then withdrawn. The furnace must be heated under such reducing conditions as will convert all the iron oxide into metal, but not allow the formation of any appreciable amount of aluminium carbide.[4] It is difficult to get the fused alumina quite free from uncombined carbon, but unless this is removed (as by a subsequent roasting in a current of air, preferably after the material has been reduced to powder) it will be difficult to unite the particles so as to form strong articles, as the carbon tends to form a " smear " over the particles and prevent the bond from reaching them.

The thermal expansion of fused alumina made from bauxite and from diaspore was found[5] to be 1·13 per cent. up to 1480° C.; at higher temperatures the material shrinks. After heating twice at 1800° C. the expansion was 1·49 per cent. The mean coefficient of expansion between 20° C. and 1750° C. is $8{\cdot}6\times10^{-6}$.

A very pure (99·9 per cent.) fused alumina made by the Thermal Syndicate Ltd. has a specific gravity of 3·97, an apparent density of 3·8, a specific heat of 0·25 (0°–500° C.), and an electrical resistance greater than that of quartz glass or porcelain. It is not affected by reducing gases, but lead, chromium, iron, and manganese oxides attack it slightly at high temperatures; so do alkalies, alkaline fluorides, and calcium and magnesium silicates.

Some of the so-called melted aluminas are merely aluminous clays, and are no more refractory that good fireclays.

Corundum, or *alundum*, is a well-known abrasive, and occurs in several localities in the Eastern United States, particularly Alabama to Maine. Corundum-syenite has been quarried extensively in Eastern Ontario, Canada, and the 6 per cent. of corundum in it is obtained by an elaborate hydraulic and magnetic process. It is made artificially by fusing bauxite or prepared

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[1] E. Ryschkewitsch, *Ber. deut. ker. Ges.*, 1930, **11**, 620.

[2] *Sprech.*, 1932, **65**, 28, 256.

[3] The bauxite should not contain more than 6 or 7 per cent. of silica.

[4] According to E. Briner and R. Senglet (*J. Chim. phys.*, 1915, **13**, 351), any Al_4C_3 formed is decomposed on heating to about 500° C. *in vacuo*, or to a somewhat higher temperature in air.

[5] *J. Franklin Inst.*, 1930, p. 104.

alumina in an electric furnace, or, as patented by M. N. Lecesne, by heating a mixture of $1\frac{1}{2}$ tons of bauxite and $\frac{1}{2}$ ton of anthracite in a blast furnace. The temperature rises rapidly under the influence of the air blast—which has a pressure of 40-inch water-column at first, and is gradually raised to 160 inches or even 400 inches water-column—and eventually any iron present is reduced to metal whilst the silica is volatilised. The blast is continued until no free carbon remains, any molten iron is run off, and the fused residue—which may be withdrawn when cool—consists of fairly pure corundum, with a specific gravity of 3·9, a hardness of 9 on Mohs' scale, and a heat conductivity about three times as great as fireclay. When mixed with fireclay it may be made into crucibles and other articles of exceptional refractoriness, the mixture showing no signs of fusion below 1950° C. Such articles are strong, but have a porosity of 9 to 12 per cent., and are useless for fusing slags and salts, though valuable for metals and alloys. The makers of refractory articles of alundum bonded with a small percentage of clay state that the melting-point of such articles is 2050° C., the coefficient of expansion 0·0000071 per degree C., the maximum crushing strength 15,410 lbs. per square inch, and the tensile strength 1700 lbs. per square inch.

Crystalline alumina exists in four, or possibly five, forms:

α-Alumina is the commonest form of alumina; it is that which is stable above 1000° C., and is also the form of the natural mineral corundum. It is trigonal, uniaxial, negative, with refractive index 1·76; the specific gravity is 3·8–4·0. The crystals of α-alumina have a hexagonal form and a lamellar habit which are highly characteristic. In the crystal-lattice of this form the O-atoms are almost in hexagonal close packing with the Al-atoms in the interstices.

β-Alumina[1] is formed by crystallisation from molten aluminosilicates and by heating alumina with an alkali in an electric furnace. Its refractive index is 1·63–1·68 and its specific gravity is 3·3. It is converted rapidly into the α-form at 1400°–1700° C., but not in the presence of alkalies.[2]

γ-Alumina, stable below 950° C. (often apparently amorphous), is produced when "precipitated aluminium hydroxide" is heated to about 900° C.

A. N. Wichel[3] has also described two other forms:

	Refractive Index.	Specific Gravity.
α-trigonal . . .	α 1·760	
	ω 1·768	3·8–4·0
β-hexagonal . . .	α 1·63–1·65	
	ω 1·66–1·68	3·3

The natural mineral forms of alumina are:

α	γ
Diaspore	Hydrargillite (gibbsite)
Corundum	Bauxite

Artificial corundum is made by inverting the γ-form (precipitate) into the α-form at a temperature well above 950° C. (an electric arc is generally used so as to produce large crystals).

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[1] According to Ridgway, Klein and O'Leary (*Electrochem. Soc.*, Preprint, 1936, pp. 70–79), the β-form is not a true allotrope, but a compound with the formula $Na_2O.12Al_2O_3$. J. B. Austin (*J. Amer. Cer. Soc.*, 1938, **21**, 351) states that β-alumina is an alkali aluminate or a mixture of this with α-alumina.

[2] J. Gallup, *J. Amer. Cer. Soc.*, 1935, **18**, 144–148.

[3] A. N. Wichel, *Microscopic Characters of Artificial Minerals*, New York, 1931.

The chief patent claims are: Hasslacher, Ger. Pat. 85,021 (1894); Werlein, French Pat. 233,996 (1895); Jacobs, Amer. Pat. 659,926 (1900); Hall, Amer. Pat. 677,207 (1901); Tone, various Amer. Pats. (1909); Hutchins, Amer. Pat. 1,310,342 (1919); and Haglund, Eng. Pat. 234,830.

Sinter-corund is a pure crystalline alumina which has been heated to vitrification at 1800° C., but not to complete fusion. The temperature and duration of heating are sufficient to produce on cooling a crystalline intergrowth with the formation of a dense mass of α-corundum. The chief properties are as follows:[1] great chemical resistivity, exceptionally high resistance to slags and fluxes; specific gravity 3·9; hardness 9; porosity *nil*; permeability to gases *nil*; thermal conductivity (400°–900° C.) 4·6–6·8 kg.-cals./sq. m./hr./°C.; thermal expansion (20°–800° C.) 80×10^{-7};[2] high resistance to sudden changes in temperature; electrical resistivity at 800° C. $3{\cdot}5 \times 10^{8}$.

Electro-corundum is a term applied to the material which has been fused in an electric furnace.

Crystalline alumina (corundum) is sold in large quantities as an abrasive under various trade-names, such as *alundum*, *aloxite*, *diamantin*, and *artificial corundum*. When these are to be used as refractory materials care should be taken to ascertain that they are free from such impurities as reduce their heat-resistance.

TABLE LII.—TYPICAL ANALYSES OF BAUXITE.

In the following analyses, very small proportions are purposely omitted so as to facilitate comparison.

District.	Lime.	Magnesia.	Iron Oxide.	Alumina.	Silica.	Titanium Oxide.	Loss.
Arles, France . .	0·6	0·7	5·1	70·4	9·0	..	14·2
Hérault, France .	1·3	0·9	5·4	65·1	14·7	..	12·6
Belfast . . .	1·7	0·2	28·7	41·3	14·5	..	13·6
Arkansas . .	..	..	9·0	54·0	3·0	2·0	32·0
Cent. Provinces, India	..	..	7·0	55·0	2·0	10·0	26·0
Remeczer, Hungary .	..	..	26·3	57·0	4·6	..	11·2

For further information on bauxite see Fox's *Bauxite* (Crosby Lockwood), London, 1927.

Iron ores—chiefly hæmatite (Fe_2O_3), magnetite (Fe_3O_4), burnt ore, and Blue Billy (a by-product consisting chiefly of iron oxide)—are occasionally used for furnace linings. Their refractoriness is much lower than that of clays and alumina, but they are largely used as a protecting lining for furnaces in which malleable iron is made, a portion of the ore being reduced and recovered in the process. In an oxidising atmosphere, ferric oxide appears to be indifferent to silica, so that siliceous bricks containing a considerable proportion of ferric oxide, when used in the flues of boilers, brewers' coppers, and similar appliances, are perfectly fire-resisting so long as the heated gas contains a large proportion of unconsumed air. The firebricks known as *Windsor bricks* are of this character, and are similar in composition to soft red sandstone.

Lime (CaO) is the oxide of calcium, and is obtained by calcining limestone, chalk, or other forms of calcium carbonate. Pure lime is an extremely refractory material, and until recently was thought to be infusible.

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[1] H. Kohl, *Ber. deut. ker. Ges.*, 1932, **13**, 13.

[2] Berlin porcelain $38{\cdot}8 \times 10^{-7}$; steatite 85×10^{-7}; mullite 43×10^{-7}.

According to O. Ruff and O. Goecke, however, when pure lime is heated to 1742° C., needle-shaped crystals begin to form at atmospheric pressure, but under reduced pressure these are only observable at temperatures above 2100° C. In both cases these crystals consist of pure lime without any trace of nitride. Lime melts at 1990° C. at atmospheric pressure, and begins to volatilise at only a few degrees above this temperature, its temperature remaining constant until it is completely volatilised. Under reduced pressure it cannot be melted, even at 2450° C. This curious result requires further elucidation. It is not improbably due to the small concentration of the lime-vapour, caused by the reduced pressure. It may, however, happen that lime combines with the nitrogen of the air at atmospheric pressure and forms a less refractory compound, though no nitride was observed in the product.

Notwithstanding its great refractoriness, lime alone cannot be of service in the production of firebricks, because if, after being heated, it is exposed to the atmosphere, it slakes and falls to powder. Hence, as a refractory material, it can only be used for lining such furnaces as allow of a continuous heat, as in certain Styrian furnaces, where it has been occasionally employed. It has also been used in making very small crucibles for melting platinum, and for parts of electric furnaces.

When mixed with clay or silica, lime forms readily fusible alumino-silicates and silicates respectively, so that such mixtures are not refractory. Curiously enough, it is very difficult to produce strong bricks by adding a little clay or silica to lime and moulding and burning the mixture.

TABLE LIII.—TYPICAL ANALYSES OF LIMESTONE.

In the following analyses, very small proportions are purposely omitted so as to facilitate comparison.

District.	Lime.	Magnesia.	Iron Oxide.	Alumina.	Silica.	Carbon Dioxide.	Loss.
Buxton . . .	55·4	0·2	0·1	0·2	0·3	43·8	..
Mansfield . .	51·4	1·4	0·5	0·3	2·0	41·6	2·8
Middleton (Derbyshire)	55·1	0·2	0·2	0·1	0·7	43·6	0·1
Bath . . .	52·9	1·2	1·2		..	42·9	..
Ketton . . .	51·6	1·9	0·9		..	43·0	..
Weldon . . .	52·8	1·7	0·3	0·6	0·1	44·5	..
Ancaster . . .	52·4	1·4	0·8		..	45·5	..
Portland . . .	53·3	0·6	0·5		1·2	42·5	1·7
North Ireland . .	55·5	0·2	0·2		0·4	43·6	..
„ Wales . .	54·9	0·3	0·4		1·1	43·3	..
South „ . .	45·6	0·5	2·6		13·9	37·4	..

Magnesia (MgO) was first patented as a suitable material for lining furnaces by C. F. Claus in 1868, but its use only became recognised as a result of Thomas and Gilchrist's basic process for steel manufacture (see S. G. Thomas's patents in 1878 and 1880). Magnesia is obtained by calcining magnesite.[1]

Magnesia prepared from magnesium chloride and from the by-products of various industries may also be used, though the cost of manufacture usually makes it more expensive than the use of naturally occurring magnesite. Thus, T. Morgan in 1880 patented the preparation of magnesia as a refractory material by adding an equivalent proportion of lime to a solution of a magnesium salt, separating, washing, and calcining the product. Unless the

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[1] Magnesite is strictly carbonate of magnesium, but the term is sometimes erroneously applied to a native magnesium silicate of a similar appearance.

precipitation is carried out with exceptional care, the magnesia will be spoiled by the presence in it of a considerable proportion of lime.

Magnesia is much easier to work than lime; it does not attack silica so readily, and is thus more suitable for furnaces in which part of the lining is to be basic and the remainder of an acid character.

According to O. Ruff and O. Goecke, magnesia behaves similarly to lime, as it cannot be fused under reduced pressure, but is distinguished from lime by being infusible at any temperature attainable, the testing apparatus fusing before the magnesia at 2437° C. The Leidenfrost phenomena observable at 2009° C. suggests, however, that the melting-point of magnesia at atmospheric pressure cannot greatly exceed 2000° C. According to Kanolt, magnesia fuses at 2800° C.

Commercial magnesia melts at a considerably lower temperature on account of the silica and other impurities always present in it.

Pure magnesia is not suitable for bricks;[1] they would be weak and friable at furnace temperatures, whereas if a small percentage (6 to 8 per cent. in all) of iron oxide, alumina, silica, etc., is present, the bricks are much stronger on account of the lower temperatures at which vitrification occurs.

Mixtures of magnesia and clay have a long range of vitrification, *i.e.* after fusion has commenced, they can be heated through a long range of temperatures before loss of shape occurs.

Magnesia is usually obtained from the natural mineral *magnesite* or *magnesium carbonate* which occurs in large quantities in various localities. It is very similar to the natural carbonates of calcium and iron, and is often associated with them, but may be distinguished by its intermediate specific gravity (3·02), as shown in Table LIV.

TABLE LIV.—NATURAL CARBONATES (T. CROOK).

Mineral.	Formula.	Specific Gravity.
Calcite	$CaCO_3$	2·72
Dolomite	$(CaMg)CO_3$	2·85
Ankerite	$2CaCO_3Mg(Fe)CO_3$	3·05
Magnesite	$MgCO_3$	3·02
Breunnerite Mesitite . .	$Mg(Fe)CO_3$	3·01–3·45
Pistomesite Sideroplesite . .	$Fe(Mg)CO_3$	3·45–3·08
Chalybite . . .	$FeCO_3$	3·88

The origin of the various deposits of magnesia appears to be very variable, and the actual succession of reactions resulting in its formation is very complex and by no means satisfactorily known.

Magnesite occurs in commercially valuable quantities in Eubœa (Greece), Vietschtal in Styria, Gömör (Hungary), Frankenstein (Germany), Ural Mountains (Russia), Sweden, Jugo-Slavia, South Australia, California, Canada, Norway, South Africa, Italy, Manchukuo, Ceylon, and Central India. It occurs in four forms, namely—

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[1] The present tendency is to use electrically fused pure magnesite to which the objections in the text do not apply.

(*a*) *Magnesite spar,* which has a crystalline structure and exhibits no particular cleavage;
(*b*) *Crypto-crystalline magnesite,* which is more compact and solid and is microscopically crystalline, but *amorphous* to the naked eye;
(*c*) *Hydromagnesite,* which is a very soft rock; and
(*d*) *Breunnerite* or *giobertite,* which contains up to 30 per cent. of iron carbonate and is of considerable commercial value.

(*a*) *Magnesite spar* or *spathic magnesite* includes all the crystalline varieties of magnesite which contain not more than 5 per cent. of lime, viz. pinolite, talcspar, bitter spar, or gioberite. It has a hardness of 4 in Mohs' scale, a specific gravity of 3·0 to 3·1, and forms glossy, colourless, white or yellowish-grey masses which sometimes exhibit a structure similar to that of marble, and may often be mistaken for it.

Spathic magnesite is principally obtained from Canada and the United States, but has also been obtained from China, Norway, Ceylon, Ural Mountains (Russia), Spain, Tragöstal, Oberdorf, and Vietsch (Styria), Eubœa (Greece), and Jugo-Slavia. In the Canadian deposits near Calumet, Argenteuil Co., Quebec, the magnesite occurs in lenticular masses, and is contaminated by streaks of serpentine and lenticular masses of dolomite, which must be removed before exporting. The deposits extend to an average depth of 125 feet, and contain about 60 per cent. of magnesite and 5 to 15 per cent. of lime. A very fine variety of spathic magnesite from Nova Scotia contains 90·8 per cent. of magnesium carbonate and only 1·6 per cent. of lime.

The principal deposits of magnesite spar in the United States occur in Washington State, to the north of Spokane in Stevens County, where the deposits resemble dolomite in texture and are up to 75 feet thick. Another deposit is 200 to 300 feet thick, and contains on an average 50 per cent. of magnesite with only 2 to 3 per cent. of lime.

In Norway, the deposits at Snarum are associated with serpentine, schist, and quartzites, but are free from lime.

The Ceylon magnesite at Randeniya Wellawaya (Uva Province) contains about 96 per cent. of magnesium carbonate and only about 1·3 per cent. of lime; it contains apatite as an impurity.

(*b*) *Crypto-crystalline magnesite* is of a more compact nature than the spathic variety; the crystals are of microscopic dimensions, and some portions of the material appear almost non-crystalline, this suggesting the term "amorphous" magnesite. The crystals are united by magnesium silicate, colloidal silica, or hydromagnesite. Crypto-crystalline magnesite is white or yellow, with a matt surface when fractured.

It usually occurs in the nodular form and resembles marble and dolomite in texture. It has a hardness of 3 to 6 on Mohs' scale and a specific gravity of 2·85 to 2·95, which is higher than marble or dolomite. It occurs principally in Eubœa (Greece), Silesia, Styria, Germany, California, India, Australia, South Africa, and Italy, and is frequently associated with serpentine and dolomitic limestone.

In Eubœa, the magnesite occurs as veins in a large belt of serpentine which stretches across the northern part of the island, and is worked to a depth of 660 feet in some places, though the average depth of the workings is not more than about 200 feet. The principal workings on the island are on the south side of the serpentine belt in the Limni-Galathki district, on the north-eastern coast round Mantudi, and to the east-south-east of Chalcis, the magnesite being conveyed to the nearest port by an aerial ropeway. These beds are the most famous and productive beds of crypto-crystalline magnesite in the world, and at one time supplied nearly half the world's demand, 50 per cent. of this going to Germany.

The Grecian magnesites seldom contain more than 6·5 per cent. of lime and on an average 92 to 98 per cent. of magnesium carbonate. The proportion of silica in some cases, as at Macedon, is 4 per cent., though usually it is less than 2 per cent.

In the United States, the principal deposits of crypto-crystalline magnesite occur on the western slopes of the Sierra Nevada in California, and in a serpentine belt in the Coast Range. The Porterville deposit in Tulare County is white, and occurs in veins up to 8 feet thick containing films of serpentine, iron oxide, and a little quartz. The mineral as sold contains about 96 per cent. of magnesium carbonate and almost 3 per cent. of calcium carbonate. The Sierra Nevada deposits are interstratified with seams of clay and shale, the magnesite occurring in beds 5 to 18 inches thick, which occupy about 4½ feet out of a total thickness of 6½ feet of clay, shale, and magnesite. Magnesium silicate—probably in the form of sepiolite—is also present, and sometimes hydromagnesite. The magnesite in this locality is not so rich as that in the coast deposits, as it contains only 77 to 93 per cent. of magnesium carbonate, up to 4½ per cent. of lime and 4 to 10 per cent. of silica. Magnesite also occurs in veins in the Sonoma, Napa, and Santa Clara Counties, the average proportion of magnesium carbonate being 85 to 97 per cent. and the lime rarely exceeding 1 per cent. The silica is usually under 2 per cent., but at Red Slide, Sonoma County, it is almost 7·67 per cent.

Most of the Californian magnesite is a beautiful white fine-grained rock with a conchoidal fracture resembling broken porcelain.

The Indian magnesite in the Chalk Hills of the Salem district of Madras occurs in veins associated with an intrusive olivine-serpentine rock which is disseminated in veins through the magnesite deposits, rather less than half the rock being magnesite. The Salem magnesite usually contains 96 per cent. of magnesium carbonate, about 1 per cent. of lime, and 1 per cent. of silica, though selected portions are considerably purer.

Magnesite also occurs in the Mysore State in veins (some of which are several feet thick) associated with serpentine and schists, the principal impurities apart from these being hornblende rock and chalcedonic silica.

The richest Australian deposits occur in New South Wales in association with red clay. These deposits are very pure, and contain about 99 per cent. of magnesium carbonate, lime being entirely absent and the silica rarely exceeding 0·5 per cent. Magnesite also occurs in veins in other parts of Australia, including Victoria—where it is found in association with old metamorphic rocks, including talc and chlorite schists—Queensland, South Australia—where it occurs in similar situations to those in Victoria and in some cases is of exceptional purity—and in Western Australia (east of Kalgoorlie), where it is associated with greenstone serpentine gabbros and talcose rock.

The South African magnesites occur chiefly in Eastern Transvaal at Kaapmuiden, the Lydenburg district, and Southern Rhodesia. They contain 95 to 97 per cent. of magnesium carbonate, are perfectly white except for specks and strata of brown fibrous serpentine and thin films of silica. The magnesite is contaminated with occasional lumps of dolomite and a considerable number of small cavities filled with quartz.

The Italian magnesites occur at Castiglioncello, Piedmont, Elba, and in the Province of Turin, in altered serpentine, and are less pure than those in some other countries, only 86 to 89 per cent. of magnesium carbonate being usually present. At Castiglioncello are large deposits of a hard, compact, and partially fusible stone, containing about 89 per cent. of magnesium carbonate.

The Elba stone contains about 85 per cent. of magnesium carbonate and 8 to 9 per cent. of silica, whilst the rock at Monterufoli, in Pisa, which occurs in a vein 4 to 8 metres thick, contains about 86 per cent. of magnesium carbonate.

The Russian magnesite occurs chiefly in the Slatoust and Orenburg districts and in Siberia. It is chiefly crypto-crystalline and contains 1·5–4 per cent. of iron oxide, so that it is intermediate in purity between the Greek and Austrian deposits and is superior to the Jugoslav ones. The Manchurian deposits are very large and in composition resemble the Russian magnesite.

(*c*) *Hydromagnesite* is a hydrated carbonate of magnesia which usually occurs as superficial deposits consisting of white chalky masses of a soft and friable character, and containing only 72 to 78 per cent. of magnesium carbonate.

The principal deposits in North America are at Atlin in British Columbia, Skagway in Alaska, Dease Bay in the Mackenzie district, where it occurs in association with dolomite, and in California, where it is associated with serpentine. The average proportion of magnesium carbonate in the British Columbia deposits is 78 per cent., that of lime, iron oxide, and silica being very low.

The chief deposit in Ceylon is in the Central Province, where it occurs in association with a metamorphosed dolomite; this accounts for its contamination with 16 per cent. of lime.

(*d*) *Breunnerite* may be regarded as a crystalline magnesite containing 5 to 30 per cent. of ferrous carbonate. It is very widely distributed, but the principal commercial source is Czecho-Slovakia, where it occurs in the metamorphosed greywacke beds of the Lower Carboniferous strata, which contain large deposits of chalybite and spathic manganese ore (rhodochrosite). The Styrian magnesites of this district—of which those from Vietschtal are the most famous—occur in lenticular masses associated with shales, sandstone, and conglomerates. Some of the masses are of great size, one at Sattlerkogels being 4000 feet long, 1000 feet wide, with a vertical working face more than 500 feet high.

The best breunnerite contains 90 per cent. of magnesium carbonate and not more than 5 per cent. of iron oxide, other impurities being talc, quartz, ankerite, calcite, pyrites, and dolomite. Breunnerite chiefly occurs as a greyish fine-grained mass or in the form of dolomitised crinoids. It also contains a large amount of yellowish dolomite of a coarsely crystalline character. This is a source of trouble in the quarrying of the Styrian magnesite, and must be separated by hand picking. Cornú also states that dolomite occurs as iron-zoned crystals lining cavities in the rock and associated with quartz, calcite, aragonite, pyrolusite, and pyrites. Some of the magnesite occurs as pinolite—a mixture of magnesite and talc schist. In general, the magnesite is of a greyish colour due to the isomorphous intergrowth of ferrous carbonate, which causes the rock to turn brown on prolonged exposure to the action of the weather. On burning, it is blackened by the reduced iron oxide.

The Styrian magnesite is of great commercial importance; it is almost wholly exported in the sintered form, only a small amount of raw magnesite being sent out of the country. About three tons of the rock produces about one ton of raw magnesite, the two tons of waste material being separated by sorting. Magnesite from inferior seams is now being purified by a system of flotation.

Breunnerite is also quarried at Trieben, Jolsva, and Nyastya, in Czecho-Slovakia.

In Canada, breunnerite occurs in Brome County and elsewhere in Quebec in association with grey mica schists containing chrome ore, mica, dolomite, and steatite. The average content of magnesium carbonate is about 83 per cent., though in some cases only about 60 per cent. is found; 8 to 32 per cent. of silica and 9 to 15 per cent. of ferrous carbonate are usually present.

In India, breunnerite occurs at Huliyar in the Mysore State in association with talc and a fibrous serpentine (picrolite), and is surrounded by crystalline schists.

Breunnerite is also found in Mount Boltscheja in the Urals, Russia. It is burned at Satka, and is used as a rife in the Russian steel industry.

Where the breunnerite contains more than 30 per cent. of iron carbonate it is useless for any commercial purpose, and for use as a refractory material, not more than 8 to 12 per cent. of ferrous carbonate should be present.

Magnesite is generally obtained by quarrying, but in some places, as at Eubœa, it is mined either by the pillar-and-stall method or by means of long-wall working. The raw magnesite should be carefully examined, and any serpentine, dolomite, quartz, as well as numerous varieties of magnesium silicate and other foreign substances removed as completely as possible. This is more especially the case when the ore contains fusible materials, or materials which can combine with it to form a vitrifiable mass.

The ore is then broken into pieces the size of a man's head. These " balls " are then examined by the " picker," who removes the foreign earths and stones as much as possible, and only sends to the works the portions which he judges to be sufficiently pure. It is, therefore, of the greatest importance that the " pickers " should be thoroughly conscientious and reliable men, as much of the success or failure of the works depends on the care and skill they exercise in the cleaning of the stone. Indeed, much of the success attending the use of the Austrian magnesite is due to the great care taken in selection, and to the efficient calcination and proper grading of the material.[1]

In order that the crude magnesite may be sufficiently refractory, it must be low in iron, silica, and alumina, and the total of these oxides should not exceed the following limits: lime, 5 per cent.; silica, 5 per cent.; alumina, 5 per cent.; iron oxide, 8 per cent.; potash and soda (alkalies), 3 per cent. In most cases, it is better if the percentages are only half those mentioned. In S. G. Thomas's patent (1880) it is recommended that if the silica is much below 5 per cent. it should be made up to this by the addition of clay, provided that such addition does not unduly increase the proportion of alumina.

The iron oxide is seldom present in the free state, but chiefly as magnesio-ferrite, $2MgO.Fe_2O_3$, or as calcium ferrite, $2CaO.Fe_2O_3$; the latter melts at 1400° C. and aids the sintering of the magnesite.

The iron oxide present is not regarded commercially as an impurity, because magnesites which are almost free from it are exceedingly difficult to sinter. The iron oxide acts as a very convenient flux, 2 to 4 per cent. being sufficient to produce a well-sintered material. A much larger percentage of iron oxide is undesirable, as it reduces the refractoriness of the product. It is of great importance that the magnesite should be almost free from lime, clay, and free silica.

The relative value of the various types of magnesite depends largely on the

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[1] There is great scope for the use of various methods of vanning, elutriation, flotation, and other well-known processes of separation of minerals in the purification of magnesite. These methods are applicable to both the raw and dead-burned material.

purposes for which they are required. The coarser varieties of magnesite—such as spathic magnesite and breunnerite—are in some ways preferable to cryptocrystalline magnesite, as when they are roughly crushed the impurities are more easily removed. Breunnerite, if not too high in iron, is one of the most desirable forms, as it loses its carbon dioxide more rapidly than the purer varieties of magnesite and is, therefore, cheaper to calcine, and the ferrous carbonate naturally present in it is more uniformly distributed than when iron ore is added artificially to a purer magnesite. Consequently, the calcined magnesite forms a dead-burned or sintered material at a lower temperature than a purer magnesite.

A further advantage of breunnerite is that (apart from the iron) the magnesite is in a purer state than in most other forms of magnesites, as the serpentine and quartz present in the latter are difficult to remove, whereas breunnerite seldom contains these impurities. For this reason, the Styrian magnesite is one of the most valuable deposits in the world, as the material can be easily quarried and cheaply burned with a local brown coal.

Other varieties of magnesite, such as those from Salem, India, and the Eubœan deposits, which are very pure, are commercially inferior to the Styrian material, because they require to be calcined at a much higher temperature.

Magnesite loses about half its weight when heated to 800° C. to 900° C., evolving carbon dioxide and forming *caustic magnesia.*

If this caustic magnesia is heated still more strongly, it becomes dense[1] and gradually vitrifies or sinters and forms a very hard igneous material known *dead-burned magnesia.* This is the material forming the chief constituen magnesia bricks, or after it has been crushed to a coarse powder it is valu for lining furnaces used in the iron and steel industries, but it is chiefly in the form of bricks, as these last longer than a tamped or rammed lining.

The dead-burned magnesia must be sorted carefully and stored under cc in a dry place.

Caustic magnesia, when mixed with water, forms a feebly plastic paste, bu dead-burned magnesia is entirely devoid of plasticity. A mixture of 1 part of caustic magnesia and 5 parts of dead-burned magnesia when worked into a paste with water is sufficiently plastic to be moulded into articles of very simple shape, though its plasticity is really feeble. It is essential that some of the caustic magnesia should be in the colloidal state, as when it has been subjected to prolonged grinding with water.

The effect of heat on magnesite consists essentially in the expulsion of the carbon dioxide and the formation of magnesia. If the temperature is sufficiently high, however, magnesium silicate, aluminate, and ferrate will be formed, and as all these substances are fusible, they tend to produce a vitrified mass.

The kilns used for burning magnesite are—

(*a*) *Shaft-kilns*, and particularly gas-fired shaft-kilns. In shaft-kilns, the raw magnesite and coal are fed in at the top and the burned magnesia is removed at the bottom. Unfortunately, magnesia has the unpleasant characteristic of falling to powder if it is shaken during the burning. Hence, a continuously acting shaft-kiln cannot be used unless it is specially modified for that purpose. If coal is used, the air must be supplied under pressure, though if a low grade of fuel is used, as in Styria, gas firing is preferable, as the product is free from admixture with ashes. Shaft-kilns designed by E. Schmatolla and A. Steiger respectively have proved excellent for burning Greek magnesite. A well-designed shaft-kiln should produce good sintered magnesia with a fuel consumption equal to 40 per cent. of the weight of the magnesia.

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[1] The specific gravity changes from 3·0 to 3·65.

In shaft-kilns, the firing has to be watched with especial care, as the tendency of the magnesia to bind into lumps and adhere to the sides of the kiln is very great, and may easily cause a stoppage of the firing. This tendency to agglutinate is greatly increased by any siliceous material which may be present in the stone, and it is on this account that the preliminary sorting and removal of the foreign material must be carried out with such care. All repairs to the kiln, which in clayworking are usually made with sand or clay, must, in the case of magnesia burning, be made with magnesia.

(*b*) *Continuous chamber-kilns* of the Hoffmann type (see Chapter II.). When a chamber-kiln is used, the raw magnesite must first be made into rough bricks (Chapter IV.), which are then burned in the kiln and are afterwards treated as dead-burned magnesia. The sole of the kiln must be covered with magnesia in order to prevent the material from being spoiled by contact with the kiln. When possible, the kiln should be lined with magnesia bricks.

The "setting" of the stone in the kiln varies, naturally, with the particular kind of kiln employed, because (except in shaft-kilns) the stone must be stacked in such a way that the hot gases can traverse it without much resistance. As the stone loses a large proportion of carbonic acid gas on being heated, the filling of the kilns is a matter requiring considerable skill, for the material shrinks and settles during the firing, and is exceedingly liable to slip and choke any air-passages which may have existed when the kiln was first filled. In order to utilise as much of the heat as possible, the top 20 to 30 inches of stone are set somewhat more closely than the rest, and every care is taken to get as much material into the kiln as is possible without unduly diminishing the draught, because even the best stone yields less than half its weight of magnesia on burning, and the ordinary magnesite rock only produces about 45 per cent. of its weight of magnesia, even when worked under the best conditions.

The advantage of crushing and briquetting the magnesite is chiefly due to the greater certainty of obtaining the material in a properly burned condition. When magnesite is burned in large lumps, it often happens that the interior is not properly calcined, so that the material has to be sorted and much of it re-burned. When made into briquettes, this treatment is not usually so necessary.

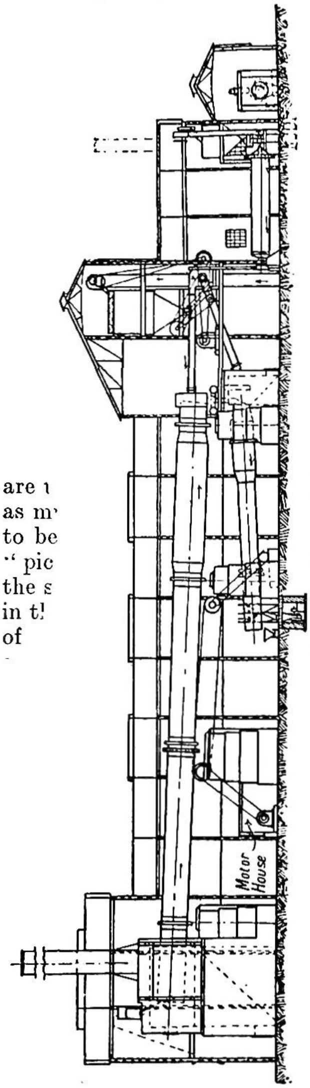

FIG. 33.—Rotary kiln.

Continuous chamber-kilns fired by producer gas and having a daily output of 10 tons have been used very satisfactorily in Styria; they require rather more fuel than a shaft-kiln, and the cost of labour in making the rough blocks and setting them in the kiln is much greater.

(*c*) *Rotary kilns* similar to those used for cement (fig. 33), and consisting of a long tube slightly inclined from the horizontal, the material travelling through this tube in one direction, whilst the burning fuel (coal-dust) and fire gases travel in the opposite one. Rotary-kilns have the peculiarity of mixing the fully burned and the partially burned material so intimately as to yield a uniform product, the quality of which is not so good as that from shaft-kilns, though it appears to be better on mere inspection. Moreover, the product is in small pieces, the surface of which is usually covered with a film of more vitrified material so that the magnesia is, notwithstanding its inferior quality, often more resistant to corrosion than the unsorted product from shaft- or continuous chamber-kilns. Rotary-kilns are also economical in fuel and labour, but are very expensive to instal, and so are not largely used for calcining magnesite, though a rotary kiln has been used very successfully at Nyristya in Czecho-Slovakia. Rotary kilns were also installed at Montreal and Hull (Quebec) in 1917, the magnesite being ground to pass through a 20-mesh sieve, mixed with 5 per cent. of ground iron ore and sintered at a temperature of 2400° C. At the works of Canadian Refractories Ltd., a calcareous, siliceous magnesite is burned in rotary kilns at a temperature of 1482°–1788° C. depending on the desired nature of the clinker. It is claimed that the rotation of the kiln causes the formation of a dense clinker of periclase crystals and dicalcium silicate, and that the particles are coated with fused silicates, which renders them inert to moisture.

(*d*) *Electric furnaces* are attractive for calcining magnesite on account of the high temperature attainable, which ensures the *complete* sintering of the purest magnesite, but they have not been used for this purpose until recently as it was found that they were not economical in producing caustic magnesia, and it was feared that to effect the preliminary calcination in a coal- or gas-fired kiln, and to complete it in an electric furnace, would be too costly, notwithstanding the superior quality of the product from an electric furnace. Experiments on a small scale by R. S. Hutton and others have shown that this double calcination ought to be economical if the plant were suitably arranged, but so far as the author is aware, the only electric furnaces used commercially for calcining magnesite are at Meraker in Norway, where electric furnaces of the Siemans and Halske type, with a current of 900 kilowatts, are employed in producing about half a ton of crystalline magnesia per day of 8 hours. The product is more fully sintered than when burned in any other type of kiln.

The temperature required to produce *caustic* magnesia on a large scale is about 800° C., and sometimes it is sufficiently burned when the maximum temperature has not exceeded 700° C. This temperature corresponds to that attained in an ordinary lime kiln. The product is a light friable material which is exceedingly porous and shrinks greatly on re-heating to a higher temperature.

The minimum temperature required to produce *dead-burned* magnesia in small quantities is that at which caustic magnesia is converted into the crystalline form (*periclase*), and if the material is finely powdered and the heating sufficiently prolonged, the conversion may be completed at about 1400° C. Parravano and Mazzetti[1] found the change to commence at about 800° C., the rate of inversion increasing with the temperature. For larger quantities, however, owing to the low thermal conductivity of the material and the necessity of avoiding an undue prolongation of the heating, the temperature to be

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[1] *Atti accad. Lincei*, 1921, 30 (i), 63–66.

attained on a commercial scale depends on the impurities present; usually it is above 1530° C. (Cone 20), and may reach to 1790° C. (Cone 36).

The fuel required for calcination is about 40 per cent. of that of the dead-burned magnesite, but it varies so much with the purity or otherwise of the magnesite, and the extent to which the latter is dead-burned, that no single figure is reliable.

The precise temperature required depends on the purity of the magnesia and on the furnace used. With breunnerite from Styria the commercially requisite temperature is 1450°–1550° C., but with some of the purer (Greek) magnesites a temperature of 1650°–1750° C. is necessary, and with a perfectly pure magnesia a temperature approaching 2000° C. would be required. If the impurities occur in bands or pockets the magnesite may also require a higher temperature for calcination than if the various materials are uniformly distributed; this statement does not apply to calcium ferrite, which when fused distributes itself readily. If a suitable flux is added to a " pure " magnesite the dead-burning temperature can be lowered 150°–400° C. The commonest flux is iron ore, but this is not satisfactory unless sufficient lime is present to form calcium ferrite ($CaO.Fe_2O_3$). When iron ore, or any other form of iron oxide, is added to magnesite, it should be in a finely ground state and should be thoroughly mixed with the magnesite. Konopicky has found that the addition of 6 per cent. of calcium ferrite ($2CaO.Fe_2O_3$) (or a mixture of finely ground lime and ferric oxide) is more effective than iron ore alone (Ger. Pat. 646,859) in magnesite low in silica. When magnesite is heated in the presence of 5 per cent. of iron oxide the first signs of softening occur at 1455° C.; if 5 per cent. of lime is also present softening occurs at 142° higher; if alumina and silica are both present the softening-point is lower. At 1450° C. the fused calcium ferrite is so mobile that it readily penetrates fairly large pieces of the magnesite and aids in sintering the mass. The addition of this substance or the equivalent proportions of iron oxide and lime or magnesioferrite has been patented (Eng. Pats. 394,115 (1931) and 399,126 (1931)). The addition of a solution of ferric chloride has proved satisfactory on a small scale. It effects a better distribution of the iron, but is regarded as too costly. The cryptocrystalline or amorphous magnesite requires a much higher temperature for calcination and is therefore more difficult to dead-burn than breunnerite or a mixture of magnesite and a flux.

Other *accelerators* are silica, alumina, various alkali chlorides, fluorspar, boric acid, etc. The addition of any flux or other accelerator reduces the refractoriness of the product and is to that extent inadvisable, except as a means of using certain kilns. In contrast to this, because a much higher temperature is attainable, the use of electricity to produce a fully dead-burned product is obviously advantageous. Konopicky has patented (Eng. Pat. 432,303—1933) the adjustment of the composition of a magnesite to within certain limits (shown on a triaxial diagram in the patent) prior to the material being burned.

The purpose of dead-burning or electric fusion of the magnesite is to convert the magnesite into magnesia, and then to cause the formation of larger crystals of magnesia (periclase) to such an extent that when the bricks are in use no further reduction in volume or increase in density can occur. Complete absence of shrinkage when in use cannot be obtained, as shrinkage is the result of a progressive series of reactions. For all practical purposes, however, the shrinkage obtainable by electro-fusion may be regarded as complete; that obtainable by other means may be sufficient, but is not complete.

The temperature attained and the duration of the heating must be sufficient to convert all the magnesia into crystalline form (periclase), or there may be trouble due to shrinkage when the magnesia is in use as a furnace lining. Many erroneous statements have been published by some persons interested in the sale of dead-burned magnesia with respect to the temperature at which it has been calcined. As already stated, breunnerite requires a lower calcining temperature than the purer forms of magnesite, and consequently some of the Styrian magnesite (breunnerite) is sufficiently shrunk by heating it to about 1410° C. (Cone 14), but in the same district a temperature 1710° C. (Cone 32) is requisite for a purer magnesite low in iron oxide, and it is generally recognised in the Vietschtal district that in no case should the finishing temperature be less than 1530° C. (Cone 20) in order to obtain a sufficiently dead-burned magnesia. The Greek and other pure magnesites and amorphous magnesite require a temperature of at least 1600° C., and some a temperature exceeding 1750° C. for complete dead-burning.

Properties of Dead-burned Magnesite.—The commercial term "dead-burned magnesite" is applied to three different materials:

(a) *Imperfectly burned magnesite,* which is unsatisfactory in use, and should be discarded or re-burned at a higher temperature. Its specific gravity is 3·0–3·3.

(b) *Sintered magnesite,* which has been heated sufficiently for the exterior of the particles to be coated with a film of fused material. The film may be of variable thickness. Sintered magnesia has a specific gravity of 3·35–3·58. It has been suggested that sintering, being more prolonged than electro-fusion, causes larger crystals to grow, so that the bulk density is affected accordingly.

(c) *Electrically fused magnesite,* which has been either completely melted or has at least been heated sufficiently to convert all the magnesia into periclase (specific gravity 3·65–3·75).

Of these three materials (c) is the best, (a) the poorest, and (b) of intermediate quality and satisfactory for most purposes. The tendency of users is, however, to impose increasingly stringent conditions and tests, so that the demand for electrically fused magnesia is likely to supersede that of sintered magnesia burned in coal- or gas-heated furnaces.

If a fairly pure magnesite (other than breunnerite) is to be burned in a fuel-heated furnace it is almost essential to add iron oxide or some other flux, or the product will shrink seriously when in use. The less pure or "mixed" material is, clearly, inferior to the electrically fused pure product, but it is much cheaper and is satisfactory except where it has to be used under the most severe conditions.

It is sometimes said that ferruginous magnesites are "preferable" to the purer ones, but the only reason for this preference is that the burning (sintering) can be effected at a lower temperature and a product sufficiently good for many purposes obtained more cheaply. "Quality for quality" the purest magnesites which have been electrically fused are the best.

Insufficiently calcined magnesia may always be recognised by its low specific gravity, and by its shrinkage on re-heating to 1580° C. (Cone 26). Raw magnesite has a specific gravity of about 3·0; this is increased to 3·38 to 3·58 on heating in a coal- or gas-fired kiln, and to 3·65 on fusing the material in an electric furnace. The specific gravity of pure periclase—the ideal product—is 3·75, but the purest electrically fused magnesite seldom has a specific gravity exceeding 3·70. The specific gravity of dead-burned breunnerite tends to be misleading, as that of magnesio-ferrite is 4·57–4·65.

Dead-burned magnesite is a hard, dense, almost inert material. The purest qualities combine slowly with water, but in those containing impurities or an added flux the particles are covered with a glassy film which protects the magnesia so that it does not slake in water. All except the most impure qualities disintegrate when exposed to steam.

The *melting-point* of pure magnesia (periclase) has not been determined with accuracy; the best determination shows 2800° C. The melting-point of breunnerite containing 5 per cent. of ferric oxide is about 2000° C.; some samples richer in iron oxide melt at 1550° C.

The *coefficient of thermal expansion* of dead-burned magnesia between 0° and 1350° C. is 42×10^{-6}. The *thermal conductivity* of electrically fused magnesia is 0·00047 C.G.S. units or practically the same as carborundum. The *electrical conductivity* of dead-burned magnesia is less than 0·34 mhos $\times 10^6$ below 1050° C., 1·0 mhos $\times 10^6$ at 1100° C., and 85·0 mhos at 1500° C., *i.e.* it is less than that of porcelain above that temperature.

The colour of the dead-burned magnesia depends on the kind of magnesite from which it is produced, or on the proportion of iron ore or other flux which may have been added. When about 4 per cent. of iron oxide is present (as in breunnerite or in a mixture of purer magnesite and iron oxide), the dead-burned or sintered magnesia is a dark chocolate brown colour; but the partially burned portions are much lighter in colour, and can thus easily be separated from the rest. The colour of purer magnesia when sintered may vary from pale yellow or buff to a light brown, according to the amount of impurities present. As the imperfectly burned material may have the same colour, it is very difficult to separate it, and for this reason the use of iron oxide as a flux, or of the natural breunnerite instead of a purer magnesite, facilitates the production of a magnesia of high quality, as the impurities and imperfectly burned magnesia may be so readily distinguished and separated.

Another property which is of importance in judging the quality of a calcined magnesite is its shrinkage when re-heated for 10 hours at 1500° C. or to such other temperatures as the maximum temperature to which the bricks will be exposed when in use. If this shrinkage does not exceed ½ per cent., the material may be regarded as having been satisfactorily burned.

The shrinkage of raw magnesite heated to 1000° C. may be 5 per cent., of that heated to 1550° C. 19 per cent., of that heated to 1650° C. 20 per cent., and of that heated to 1760° C. 22 per cent. In other words, the shrinkage varies with the temperature and duration of heating. On reheating at a higher temperature (as when in use) a further shrinkage may occur. It is, therefore, advisable to carry out a reheating test on all dead-burned magnesite as well as to determine the specific gravity, in order to ensure that the material has been properly burned.

Impurities.—Pure magnesite when heated is first converted into the α- or caustic magnesia,[1] which has a specific gravity of 3·0; as the temperature rises this is gradually converted into the β-magnesia or periclase (MgO), which is the form stable at high temperatures, with a specific gravity of 3·7–3·75 and a melting-point of 2800° C. (the precise temperature is uncertain). Commercial dead-burned magnesites consist essentially of magnesia, partly in the α-form, but chiefly in the form of periclase together with various impurities, the chief of which are lime, silica, and iron oxide. During dead-burning and when the magnesite is in use these impurities form forsterite ($MgO.SiO_2$), monticellite ($MgO.CaO.SiO_2$), spinel ($MgO.Al_2O_3$), fayalite ($2FeO.SiO_2$) and magnesium ferrite or iron spinel ($MgO.Fe_2O_3$). Iron oxide

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[1] J. W. Mellor, *Trans. Cer. Soc.*, 1917, **16**, 88.

in small proportions (3–10 per cent.) is not a serious impurity,[1] but lime and silica are objectionable as they form fluid silicates with relatively low melting-points and greatly reduce the strength of magnesia bricks in which they are present. When much silica is present, dicalcium silicate ($2CaO.SiO_2$) forms and as this disintegrates on cooling it tends to break down the whole mass. A magnesium-calcium silicate containing 20 per cent. of magnesia, 30 per cent. of lime, and 50 per cent. of silica has a melting-point of only 1350° C.

H. E. White [2] has shown that monticellite and dicalcium silicate or monticellite and forsterite may occur, but not all three minerals. He also found that if forsterite occurs in a fused magnesite, dicalcium silicate cannot also be present. Akermanite and spinel may also occur, but he did not find any enstatite or clinoenstatite.

The compounds and eutectics between magnesia and silica are high-melting substances (1850°–1890° C.), with the exception of a eutectic between clinoenstatite ($MgSiO_3$) and cristobalite (SiO_2) which melts at 1543° C.[3] Unfortunately any silica present usually forms much less refractory products with any lime or iron oxide present, as described above. A small proportion of lime appears to be essential as, without it, magnesium ferrite is not readily formed. When dicalcium ferrite is formed it produces a eutectic with magnesia which melts at 1380° C., so that the whole mass can sinter at or slightly below 1400° C.

In mixtures of magnesia and iron oxide heated to 1500°–1550° C. a eutectic melting at that temperature is formed. This and the silicates which are molten at this temperature form a viscous fluid which, instead of assisting, seems to hinder the formation of crystals of periclase.

On slowly cooling a properly sintered or fused mass, the periclase crystallises and the magnesium ferrite occupies the interstices forming a moss-like pattern.

The proportion of the various impurities present in a sample of dead-burned magnesia can best be ascertained by means of a chemical analysis, and their effect by determining the refractoriness of the material. Incompletely burned magnesite need not be regarded as useless, as some material with a specific gravity of 3·2 is quite satisfactory for use at lower temperatures than those to which the best bricks are exposed. For an accurate determination of the various minerals present, a micropetrological examination is essential. This usually requires a considerable amount of time.

Dead-burned magnesia should be stored in a dry place free from all moisture, as it tends to form magnesium hydroxide if exposed to moist air or water.

Some users require dead-burned magnesia which has been burned two or three times. This is unnecessary if the first burning has been adequate and at a sufficiently high temperature. The reheating of dead-burned magnesia after grinding it to powder was patented in 1931 (Eng. Pat. 413,905).

In order to secure a product of sufficiently high quality, the lumps of magnesia should be sorted as they come from the kiln; the material should then be passed through a stone-breaker and again carefully examined.[4]

The use of ultra-violet light (properly screened) greatly facilitates the sorting, as it shows up the impurities.

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[1] It is often added to facilitate the dead-burning (p. 220).

[2] *J. Amer. Cer. Soc.*, 1938, **21**, 216–229.

[3] N. L. Bowen, *Amer. J. Sci.* (4), 1914, **38**, 207.

[4] See footnote on p. 216.

Table LV.—Typical Analyses of Magnesite.[1]

In the following analyses, very small proportions are purposely omitted so as to facilitate comparison.

<table>
<tr><th>District.</th><th>Lime.</th><th>Magnesia.</th><th>Iron Oxide.</th><th>Alumina.</th><th>Silica.</th><th>Carbon Dioxide.</th><th>Loss.</th></tr>
<tr><td>South Africa . .</td><td>..</td><td>45·3</td><td>0·8</td><td>..</td><td>2·3</td><td>49·8</td><td>0·2</td></tr>
<tr><td>Atlin, Canada . .</td><td>2·1</td><td>41·1</td><td>0·8</td><td>0·7</td><td>1·9</td><td>36·0</td><td>18·0</td></tr>
<tr><td>Mysore, India . .</td><td>0·4</td><td>47·1</td><td colspan="2">0·1</td><td>..</td><td>52·9</td><td>..</td></tr>
<tr><td>Salem, „ . .</td><td>0·3</td><td>46·3</td><td>0·2</td><td>0·3</td><td>0·2</td><td>51·9</td><td>..</td></tr>
<tr><td>N.S. Wales . .</td><td>..</td><td>47·1</td><td colspan="2">0·5</td><td>0·4</td><td>51·9</td><td>..</td></tr>
<tr><td>Queensland . .</td><td>1·5</td><td>46·9</td><td colspan="2">0·2</td><td>0·2</td><td>51·3</td><td>..</td></tr>
<tr><td>S. Australia . .</td><td>0·2</td><td>46·2</td><td>0·4</td><td>0·6</td><td>1·0</td><td>51·0</td><td>0·5</td></tr>
<tr><td>Mittendorf, Styria .</td><td>1·7</td><td>42·4</td><td>3·9</td><td>0·4</td><td>0·9</td><td>49·3</td><td>1·4</td></tr>
<tr><td>Vietsch, „ .</td><td>1·3</td><td>42·9</td><td>3·5</td><td>0·3</td><td>1·9</td><td>47·3</td><td>2·8</td></tr>
<tr><td>Breitenau, Austria .</td><td>2·8</td><td>41·3</td><td>5·5</td><td>0·7</td><td>2·0</td><td>46·6</td><td>..</td></tr>
<tr><td>Salsburg, „ .</td><td>2·0</td><td>40·9</td><td>5·9</td><td>1·1</td><td>2·2</td><td>45·0</td><td>..</td></tr>
<tr><td>Eubœa, Greece .</td><td>2·4</td><td>45·1</td><td>0·8</td><td>..</td><td>0·5</td><td>50·7</td><td>0·5</td></tr>
<tr><td>Mantudi, „ .</td><td>0·5</td><td>46·7</td><td colspan="2">1·2</td><td>0·3</td><td>51·7</td><td>..</td></tr>
<tr><td>Macedon „ .</td><td>1·1</td><td>47·0</td><td colspan="2">0·4</td><td>2·5</td><td>52·6</td><td>..</td></tr>
<tr><td>Kymi, „ .</td><td>3·4</td><td>43·8</td><td colspan="2">0·5</td><td>1·3</td><td>50·9</td><td>..</td></tr>
<tr><td>Gömör, Hungary .</td><td>1·7</td><td>42·4</td><td>..</td><td>4·3</td><td>0·9</td><td>50·4</td><td>0·3</td></tr>
<tr><td>Frankenstein, Germany</td><td>0·6</td><td>46·2</td><td>1·1</td><td>0·4</td><td>4·5</td><td>46·1</td><td>1·1</td></tr>
<tr><td>Ural, Russia . .</td><td>0·9</td><td>46·1</td><td>1·6</td><td>..</td><td>0·3</td><td>51·1</td><td>..</td></tr>
<tr><td>Pisa, Italy . .</td><td>5·4</td><td>40·9</td><td colspan="2">2·63</td><td>1·1</td><td>42·3</td><td>..</td></tr>
<tr><td>Castiglioncello, Italy</td><td>2·8</td><td>42·4</td><td>2·0</td><td>..</td><td>3·0</td><td>48·8</td><td>..</td></tr>
<tr><td>Paturkorso, Sweden .</td><td>4·6</td><td>34·8</td><td>10·9</td><td>..</td><td>4·1</td><td>44·3</td><td>1·3</td></tr>
<tr><td>Snarum, Norway .</td><td>..</td><td>47·3</td><td>0·8</td><td>..</td><td>..</td><td>51·5</td><td>..</td></tr>
<tr><td>Portville, U.S.A. .</td><td>1·1</td><td>46·0</td><td>0·2</td><td>..</td><td>0·8</td><td>51·3</td><td>..</td></tr>
<tr><td>Napa Co., „ .</td><td>1·6</td><td>43·7</td><td>2·4</td><td>..</td><td>2·4</td><td>50·1</td><td>..</td></tr>
<tr><td>Washington „ .</td><td>0·3</td><td>46·2</td><td>1·0</td><td>..</td><td>0·5</td><td>50·3</td><td>..</td></tr>
</table>

The dead-burned magnesia may be partially purified by moistening it with water or steam, and, after standing for a couple of days, passing it through a perforated drum. Any lime present is thereby hydrated, falls to a powder, and passes away through the openings of the drum, whilst the magnesia remains in a coarser form and is thus easily separated.

For use, the *caustic* magnesia is usually ground in a ball mill or pendulum mill similar to those used for Portland cement. The *dead-burned* magnesia is first crushed in a stone-breaker and ground in a ball mill, fitted with an air-separator (fig. 42), to a coarse powder, like grog. An edge-runner mill and screen is not satisfactory, as it is necessary to enclose the whole in a dust-proof case. Edge-runner mills are sometimes used for grinding the material under water (wet-grinding), some firms preferring this to a dry-grinding process. The grains should be less than $\frac{1}{16}$ inch in diameter, but no dust should be present.

As the dust created by grinding magnesia is highly detrimental to health, it is important to use effective dust-collecting appliances.

The ground clinker greatly resembles emery both in colour and sharpness, and is extremely dangerous to the workmen employed in its production. Its hardness is so great that it rapidly wears away the grinding surfaces of the machinery, so that its production is apt to be costly if cheap machinery of soft iron or very mild steel is used for its reduction.

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[1] For convenience, the terms "Styria," "Austria," and "Hungary" are retained.

Dolomite is the incorrect, but common, name for the magnesian limestone used in lining steel converters in accordance with Thomas and Gilchrist's basic process, and for open-hearth steel furnaces. It has the advantage of being more durable and economical than limestone, though the latter can be purchased more cheaply.

The most important magnesian limestones in England occur chiefly in the Permian system, and appear to have been formed from normal limestones by the action of water containing magnesium carbonate in solution, though some are considered to have been formed by *bryozoa*. They outcrop at Nottingham, and run through Mansfield, Worksop, Doncaster, Brodsworth, Pontefract, Tadcaster, and Darlington, the area then extending to Hartlepool, Sunderland, and South Shields. Near Mansfield, the best portions rise in small hillocks protruding from the surrounding Permian beds.

For dolomite bricks, the best sources of material are Mansfield Woodhouse, Bolsover Moor, Steetley near Worksop, North Anston, Roche Abbey, Huddlestone, Brodsworth, Cadeby, and Kiveton Park, the last six all being in South Yorkshire. Some of the Mansfield stone is too siliceous to be used for furnace work.

A true dolomite has been quarried for many years by the Steetley Lime and Basic Co. Ltd., of Worksop, Notts, and small quantities of true dolomite are found elsewhere, but the greater part of the magnesian limestone is not a true dolomite. If the material is carefully selected, so that the proportions of magnesite and calcite are roughly the same as those in true dolomite, the commercial use of magnesian limestone as a refractory material appears to be as satisfactory as that of true dolomite.

The colour of the dolomite ranges from pale cream to yellowish brown; and the freshly broken surfaces have a crystalline sparkle or sugary effect. Minute specks of iron oxide are common, but the total percentage of this substance is usually small.

Dolomite rocks require to be selected with special care, as they are liable to rapid variations in the beds.

Dolomite may be readily distinguished from common limestone by its—

(1) Being very feebly attacked by cold hydrochloric acid.
(2) Superior hardness.
(3) Greater specific gravity (2·8 to 2·9).
(4) High content of magnesia.

Under the microscope it is often difficult to distinguish the crystals of dolomite from those of calcite, as the two are very similar. Dolomite, however, shows a slightly yellowish tinge, and the crystals have rhombohedral outlines with colour zoning.

Magnesia is a much better material for furnace linings than magnesian limestone, though the latter is much cheaper in first cost. When durability is taken into consideration, however, magnesia bricks prove so superior to dolomite that they are rapidly replacing the latter.

True dolomite is a definite mineral with a definite composition corresponding to $CaMgC_2O_6$, whereas the proportion of calcium and magnesium carbonate varies in magnesian limestone.[1] The composition of natural minerals classed as dolomite varies considerably, the range in composition being from 28 to 35 per cent. lime, 14 to 20 per cent. magnesia, 1 to 7 per cent. silica, 0 to 14 per cent. alumina, 0·5 to 5 per cent. ferric oxide, and 43 to 46 per cent. carbon dioxide.

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[1] If a piece of magnesian limestone is examined, the proportion of crystals of dolomite present will usually show whether the specimen should be termed a dolomite or merely a magnesian limestone.

Strictly, the term " dolomite " should be restricted to the double carbonate $MgCO_3.CaCO_3$ which, on analysis, shows 21¾ per cent. of magnesia, 30½ per cent. of lime, and 47¾ per cent. of carbon dioxide.

In his 1870 patent, S. G. Thomas advised that, for making dolomite furnace linings or dolomite bricks, a magnesian limestone be selected which contains not more than 7 per cent. of silica, and 5 per cent. of oxide of iron and alumina. It should also contain about 33 per cent. of lime, 18 to 20 per cent. of magnesia, and 42 to 46 per cent. of carbonic acid. This is broken into fragments and burned at as high a temperature as possible in a shaft-kiln charged with alternate layers of dolomite and coke, and using an air-blast. The material is then ground in an edge-runner mill until it will all pass through an opening ¾ inch in diameter. For furnace linings, this ground material is mixed with tar or pitch, sufficient to form a " slurry," or thin pasty mass. This is run into a mould of the required size and shape, then consolidated by heat, or a somewhat stiffer paste made of the same materials is rammed into position in the furnace so as to form a lining.

In the early days of calcining dolomite the temperatures attained seldom produced a true *dolomite clinker* or properly *sintered dolomite* in which all the magnesia was converted into periclase; this requires a very high temperature (approaching 1700° C.) unless the stone is very impure. It is now recognised that the more complete the fusion of the dolomite the better will be the quality of the product.

In this country, chiefly shaft-kilns are employed for burning dolomite, but in the United States, rotary kilns are also used. Rotary kilns are stated to effect the sintering at a lower temperature and, owing to the very thorough mixing of the ashes, etc., with the dolomite during the rotation of the kiln, the pea-shaped fragments are coated with a slag-like material which prevents rapid deterioration of the lime; as a result of this, dolomite which has been burned in a rotary kiln may be used 8 to 10 weeks after calcining; this would be unwise with that burned in a shaft-kiln, as in the latter the presence of lime and impurities is more marked, and, consequently, it is usually easy to pick the greater part of the dolomitic lime and so separate it from the ash and other impurities.

Prior to calcining in a rotary kiln the dolomite should be crushed to pieces about 1 in. cube and all fine powder should be removed. In a shaft-kiln the pieces should be 2–4 in. in diameter and as uniform as possible in size. Electrically fused dolomite is much superior to that burned in any type of fuel-heated kiln.

The dolomite should be burned at an " intense white heat " so as to form a compact, hard, and highly shrunk material. The temperature required for this is similar to that needed for the dead-burning of magnesia. In the method patented by Thomas and Gilchrist in 1880, a cupola or blast furnace with a basic lining is filled with coke to a height of about 5 feet above the tuyères, and equal volumes of coal and dolomite in small lumps are then added. The hot blast is turned on and charging continued until the cupola is full of shrunk dolomite, viz., after about six hours. After all the coke has burned away, the bottom of the cupola is removed and the sintered product withdrawn by iron pokers. The heating must be maintained for a sufficient time to shrink the dolomite thoroughly, or it will be useless.

The fuel required for calcining dolomite varies from 50 to 200 per cent. of the weight of the calcined product.

Although complete dead-burning can scarcely be attained in fuel-fired furnaces,[1] the selected product of well-designed coke-fired furnaces has been used with satisfaction for many years in the Steel Trade, notwithstanding the fact that it is not completely dead-burned.

The first effect of heat on dolomite is to form a mixture of calcium carbonate and magnesia with evolution of half the carbon dioxide in the dolomite (the calcium carbonate being decomposed only at a still higher temperature) forming a mixture of lime and magnesia. If silica is present, however, it may combine with the magnesia and form forsterite, Mg_2SiO_4 (which may decompose and form serpentine), or with the lime and form wollastonite, $CaSiO_3$, or other silicates. With an excess of silica, pyroxenes such as $CaMgSi_2O_6$ may be formed. When alumina is present, spinels may be produced, the magnesium aluminates forming more easily than the calcium aluminates. In the presence of both silica and alumina, a mixture of calcium carbonate, forsterite, and magnesium spinel may be formed, and various silicates if the temperature is sufficiently high. If sufficient silica is present, it may form with the lime a dicalcium silicate which disintegrates on cooling, but the combination of lime with alumina, on the contrary, provides a stable calcium aluminate (spinel).

According to Weyl, calcium ferrite is not formed in the presence of an excess of magnesia except at very high temperatures, so that the addition of iron oxide does not render the lime harmless.

Dead-burned dolomite which contains an unsuitable proportion of silica either slakes or disintegrates. Dolomite with at least 0·5 per cent. of iron oxide and less than 6 per cent. of silica slakes and breaks down in the presence of moisture; that with the same proportion of iron oxide and more than 9 per cent. of silica disintegrates on cooling owing to the presence of dicalcium silicate, $2CaO.SiO_2$. F. E. Lathe[2] maintains that the lime : silica ratio should lie between 1 : 1·4 and 1 : 4·0. The presence of the small proportion of iron oxide as well as a restricted proportion of silica appears to be essential to stability, but alumina, if present, has the same effect as iron oxide. The most stable dolomite contains (approximately) iron oxide 6 per cent., silica 7–8 per cent. and dolomite 86–87 per cent. A larger proportion of iron oxide does little harm beyond lessening the fusion-point of the mixture. A little iron oxide is, therefore, added to some pure dolomites which are calcined in shaft- or rotary-kilns in order to increase the amount of sintering, though at the expense of the refractoriness of the product.

Most commercial dolomite slakes readily on exposure to moist air or water, because it is deficient in silica. To prevent it from slaking the pieces of burned dolomite may be coated with wax[3] or other inert waterproof material, but as such treatment is expensive it is better to use the dolomite in a freshly burned state or, if it must be stored, keep it in air-tight bags in a dry place.

The use of dolomite which has been burned at a temperature "below white heat" was patented by Saml. Pitt in 1879, and by several other people since that date.[4] The chief objection to its use is the great shrinkage and loss of shape when bricks made from it are burned at a suitable temperature, or the great shrinkage if under-burned bricks are employed.

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[1] It is comparatively easy in an electric arc-furnace.

[2] *Chem. Eng. Cong. World Power Conf.*, B.1, 1936.

[3] Longbottom, Duffield and Rees, Eng. Pat. 191,412 (1921).

[4] Many of these patents are useless, but that of Albert P. Meyer (U.S. Pat., 1915, 1,160,085) is interesting historically, as it suggests a mixture of dolomitic lime and basic slag as a substitute for magnesia bricks, "now that these are scarce on account of the war."

Properties.—Dead-burned dolomite consists essentially of a mixture of lime and magnesia, and if the material is very pure it will be friable, as there is no bond to give it strength. Burning at the highest temperatures attainable in a fuel-fired furnace will not form a strong product in the absence of a bond. This was the cause of many difficulties until the origin of the weakness was discovered. With less pure dolomite or with a mixture of dolomite and a flux, the dead-burning produces a mass in which the particles are covered with a glassy film of fusible silicates which causes them to adhere to each other. The various substances present are the same as in dead-burned magnesia (p. 222), though in different proportions, and the presence of a large proportion of lime tends to produce a more mobile and more easily fusible glass than that present in dead-burned magnesia. Another difference is the much smaller proportion of ferrites, except in those dolomites to which iron ore has been added as a flux (p. 227). Dolomite is exceedingly difficult to dead-burn satisfactorily, as the size of the pieces, the nature of any fluxes present or added, the temperature and the duration of heating all affect the product. With sufficient care in blending, it is practicable to produce grains of dead-burned dolomite of suitable size which will neither slake nor disintegrate even in an autoclave, and yet have a refractoriness greater than Seger Cone 32 (1710° C.). (See Eng. Pats. 450,961—1934 and 492,565—1937.)

To ensure this the dead-burned dolomite should not contain more than 7 per cent. of silica, 3 per cent. of alumina, or 6 per cent. of ferric oxide. With very pure dolomite the rate and the extent of the slaking are independent of the temperature of the dead-burning, but any impurity present and any addition of iron oxide or other flux tends to lessen the rate of hydration, because of the formation of a molten glass which coats the particles of dolomite.

The *melting-point* is indefinite and varies with the composition of the material. The most fusible mixture of pure lime and pure magnesia melts at 2300° C. and contains 35 per cent. of magnesia and 65 per cent. of lime. Perfectly pure dolomite melts at about 2500°–2800° C., but some commercial dolomites show signs of fusion at 1500° C., though complete loss of shape may not occur below 1900° C.

Shrinkage.—Raw dolomite has a volume-weight of 2·7, but when heated at 800°–1200° C. for some time the volume-weight sinks to 1·4–1·5, and on heating to 1500° C. or above (*i.e.* on sintering) it rises to 2·8–3·0. Good commercial dead-burned dolomite has a volume-weight of at least 2·9. Dolomite which has been insufficiently heated shrinks greatly when in use; in some instances shrinkage of 50 per cent. has been recorded. The only means of minimising this consists in effecting the dead-burning at a sufficiently high temperature and for a sufficiently long time; iron oxide or other flux may be added, prior to burning, if the dolomite is very pure and the heating has to be restricted.

Under-burned dolomite may be mixed with the dead-burned product; but little or no advantage is gained, as the bricks must then be burned at a sufficiently high temperature to shrink the raw stone completely, or the bricks will contract unduly when in use, and this may cause serious damage.

Slaking and Disintegrating.—Fully sintered dolomite does not slake readily on exposure unless finely ground, so that ready slaking is usually a sign of insufficient burning.

Dead-burned dolomite is liable to two serious defects:

(i) it slakes on exposure to moisture as a result of the hydration of the free lime present; or

(ii) it disintegrates during or soon after cooling as a result of the presence of β-dicalcium silicate (p. 227), which is transformed automatically into the γ-form with an increase in volume of about 10 per cent.

These defects are best minimised (they cannot be wholly avoided) by (*a*) using a raw stone containing at least 0·3 per cent. of iron oxide (or adding iron ore to make good the deficiency); (*b*) restricting the silica to 5–9 per cent., as smaller and larger proportions of silica will increase one or other of these defects; and (*c*) burning at a higher temperature or fusing electrically.

Impurities.—The chief difficulties arising in the use of dolomite are due to the material being "too pure," with the result that it is weak and it also slakes readily. Impure dolomites, on the other hand, are not satisfactory because they contain an excess of silica (see "Disintegration"). The best procedure is to select an almost pure dolomite and to "improve it" by one of the following methods:—

(i) Reducing its tendency to slake on exposure to moist air or to water. This is usually effected by adding iron oxide and silica or clay (or alumina) to the raw dolomite so as to form a molten glass which will coat the particles and render them waterproof. If the added matter contains much silica it may form dicalcium silicate and disintegrate the dolomite.

(ii) Causing the dolomite to sinter at a lower temperature and so allow a more complete dead-burning. This is effected by adding a flux such as iron oxide or alumina. Clay, flue dust, and other substances containing silica should not be used. They are liable to cause disintegration by formation of dicalcium silicate and they reduce the refractoriness of the dolomite.

(iii) Increasing the refractoriness by removing most of the lime (see "Decalcification").

Decalcification.—Many attempts have been made to improve dolomite by removing the greater part of the calcium carbonate present. The following methods are technically available, but the purified product is usually too costly[1] to compete with dead-burned magnesia, for which it is, after all, an indifferent substitute:—

If a lightly burned dolomite is sprayed with a small excess of water, the latter will combine with the lime much more rapidly than with the magnesia and the slaked lime will fall to powder. The coarser pieces can then be separated by a screen or sieve and will be much richer in magnesia. This method does not completely remove the lime, but the product is useful where dead-burned magnesia is not available (see also Eng. Pat. 1425—1907).

The lightly calcined dolomite is slaked with water and is afterwards saturated with carbon dioxide, which precipitates calcium carbonate whilst magnesium bicarbonate remains in solution. After filtration to remove the lime, the solution is boiled and the magnesium carbonate collected, dried, and re-burned. It is difficult to obtain a product containing more than 85 per cent. of magnesia.

One method of treatment (Eng. Pat. 471,373—1937) consists in treating the burned dolomite with ferrous chloride and re-burning. The cost is probably prohibitive. In Ger. Pat. 335,349 (1931) L. Altman claims that by treating burned dolomite with a solution of magnesium chloride the lime is washed out in solution as chloride and the magnesia is precipitated. By

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[1] The British Periclase Co. Ltd. was, in 1939, producing magnesite bricks from dolomite from which much of the lime had been separated, and then claimed that the process used was commercially satisfactory.

this means a calcined dolomite containing only 36 per cent. of magnesia can be made into one containing 70 per cent. of magnesia (see also Eng. Pats. 363,871—1931 and 471,234—1937).

A method devised by Scheibler, used for many years at Hörde, was finally abandoned as being too costly, though the product was excellent. The dolomite was burned and then made into a milk with water. Into this, water containing 10 to 15 per cent. of molasses was poured, and the liquids mixed thoroughly. The lime formed a soluble saccharate, whilst the magnesia remained in suspension and was filtered off. The solution was then treated with carbon dioxide, which precipitated the calcium carbonate, and the molasses liquor was re-used. The loss in molasses was 10 per cent.

A cheaper and more practicable process is Closson's, which consists in mixing magnesium chloride with "milk of dolomite-lime." The reaction takes place rapidly, forming soluble calcium chloride and insoluble magnesium hydrate; the latter is separated in a filter press, washed and used. The liquid is mixed with freshly burned dolomite, and flue gases are passed through it. The magnesium chloride is re-formed and the liquor is used over again, the mud being thrown away. There is a loss of about 6 per cent. of magnesium chloride, so that to make 1 ton of magnesia, 3000 lbs. of dolomite and 2000 lbs. of magnesium chloride are required. The cost of treatment (magnesium chloride being a by-product) is ten shillings per ton. The product contains 97 per cent. magnesia, 2 per cent. lime, and 1 per cent. iron oxide, and is quite satisfactory as a refractory material.

TABLE LVI.—TYPICAL ANALYSES OF DOLOMITE.

In the following analyses, very small proportions are purposely omitted so as to facilitate comparison.

District.	Lime.	Magnesia.	Iron Oxide.	Alumina.	Silica.	Carbon Dioxide.	Loss.
Mansfield (Yellow)	28·2	20·2	0·4	0·3	3·3	45·1	2·5
,, (White)	14·8	8·6	0·7	0·6	51·4	21·1	2·8
Sunderland	29·4	19·6	0·7	0·8	4·3	45·2	..
Doncaster	31·6	19·7	0·5	0·4	1·1	46·5	0·2
Cumberland	36·3	10·9	16·1	0·9	0·6	34·4	..
Issining, New York	29·1	17·8	0·2	trace	10·6	42·5	..
Cerro Gordo, California	49·3	5·7	0·1	..	0·1	44·7	..
Frankenstein, Germany	15·1	32·3	3·7	0·7	0·1	47·5	..
Switzerland	27·4	19·2	0·5	..	10·9	42·7	..
Gerolstein, Germany	29·6	21·1	0·8	0·2	1·2	46·6	..
Tyrol	27·8	11·7	2·4	23·4	0·1	34·7	..
Carinthia	30·6	21·5	trace	0·3	0·2	47·7	..
New Almadin, California	35·6	21·5	8·6	trace	0·4	46·4	..
New York	33·6	12·6	2·4	..	0·3	40·2	..
Missouri	31·7	19·7	1·2	0·6	0·2	46·6	..

Both these processes have the disadvantage of requiring large amounts of "chemicals" and are, therefore, costly. Cheaper methods, which yield an inferior magnesia, are: (*a*) A. M. Mitchell's method of heating the crushed dolomite to a temperature of about 500° C., which he presumes to be sufficient to convert the magnesium carbonate into oxide but not to affect the calcium carbonate; the product is then treated with water or in a pneumatic separator so as to separate the fine particles of magnesia from the coarser unaltered material. (*b*) Hardy and Isham's process, in which the dolomite is calcined at a much higher temperature so that both are decomposed; the lime is then extracted with water on account of its greater solubility than magnesia, and the residue, after drying, is ready for use. The process can be repeated until only 5 per cent. of lime remains; but if a large proportion of lime is present, the process would scarcely be profitable. (*c*) A similar process has been patented by A. S. Davidson & Co. (U.S. Pat. 1,270,819), in which the material is calcined in a rotary kiln at a temperature just sufficient to drive off the carbon dioxide, the product being crushed to the size of peas and sprinkled with water, which slakes the lime, causing it to fall to powder, so that it may easily be removed from the coarser unaltered magnesia by screening. The patentees claim to be able to separate all but about 3 per cent. of the lime.

A. Braconnier, in 1880, patented a method of removing the lime by heating the limestone with a solution of ammonium chloride, which dissolves the carbonate, but does not affect the magnesite. The latter is drained, washed with water, and burned to convert it into magnesia. Another method consists in treating a dolomite with carbonic acid solution, which removes the calcium carbonate before the magnesium carbonate.

Other chemical methods[1] of separation include:

Closson's method, as altered by Robinson (Canad. Pat. 201,398—1920), using calcium chloride.

Clerc's method (Eng. Pat. 173,502—1921), which slakes only the calcium oxide.

Delage's method (Eng. Pat. 134,626—1918), in which the raw dolomite is treated with sodium bisulphate and the resultant sodium magnesium sulphate is electrolysed and magnesia liberated (see also *J. Franklin Inst.*, 1920, **190**, 739).

Twyman's method (Eng. Pat. 317,961—1928), in which raw dolomite is treated with nitric acid, burned dolomite added, and the magnesium hydroxide separated from the calcium nitrate.

Barrett's method (U.S. Pat. 1,816,996), in which dolomite lime is treated with ammonium chloride.

Bradburn's method (U.S. Pat. 1,156,662—1915).

Platzmann's method[2] consists in suspending dolomite lime in a solution of potassium bicarbonate and passing in carbon dioxide. A soluble double salt ($MgCO_3.KHCO_3.H_2O$) is formed, whilst calcium carbonate remains insoluble. The filtered solution is boiled and magnesium carbonate is then precipitated and collected.

Physical methods of separation include:

(i) Auzies and Segoffin's method (Eng. Pat. 1425—1907), in which dolomite lime is treated with water in levigating tanks and the magnesia content increased to 80 per cent.

(ii) Mitchell's method (U.S. Pat. 1,237,110—1918), calcining at 540° C. (the method of separation is not described).

(iii) Stubbs' method (*J. Franklin Inst.*, 1920, **190**, 739), treatment with running water to remove lime from dolomite lime.

(iv) Eyoubs' method (*Eng. Min. J.*, 1921, **112**, 619), in which the dolomite lime is shaken for ten minutes with water to increase the magnesia content to 80 per cent.

So far as the author is aware, none of these processes is commercially profitable, though they form a basis for further investigation.

[1] I. I. Fränkel, *J. Chem. Met. Min. Soc. S. Africa*, 1937, **38** (6).

[2] *Cem. Lime Manuf.*, 1937, pp. 325–8.

The principal uses of dead-burned dolomite are: (i) in lead furnaces where the slag is of a highly basic character, (ii) in copper smelting furnaces, (iii) in basic open-hearth steel furnaces and Bessemer converters, and (iv) in crucibles for melting special metals and alloys.

THE OLIVINES.

The olivines form a series of (magnesium) orthosilicates with the general formula $2RO.SiO_2$, of which the simplest member is *forsterite*, $2MgO.SiO_2$ (melting-point 1910° C.), but the commonest is *olivine*, $MgO.FeO.SiO_2$ (melting-point 1600° C.). The term is applied to *forsterite*, Mg_2SiO_4, *monticellite*, $CaMgSiO_4$, *chrysolite* or *peridote*, $MgFeSiO_4$, *fayalite*, Fe_2SiO_4 (melting-point 1205° C.), and sometimes to calcium orthosilicate Ca_2SiO_4. The olivines occur as the characteristic minerals in many basic rocks, particularly in basalt, peridotites, gabbros, trachytes, and andesites.

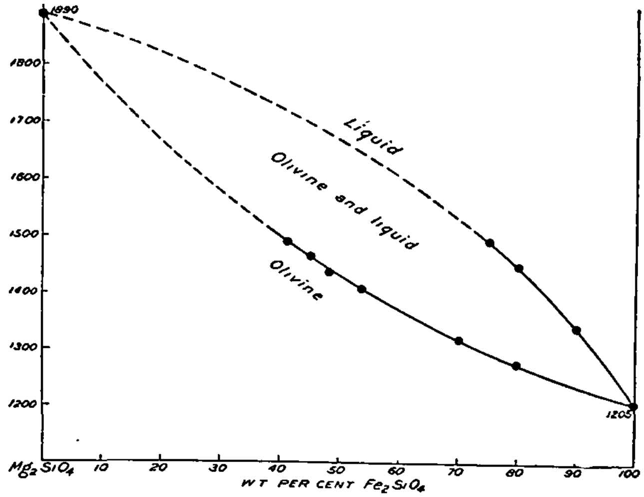

FIG. 34.—Equilibrium Diagram of Olivine System.[1]

The most suitable natural materials for making olivine bricks are the igneous rocks known as *dunites*, which contain about 40 per cent. of silica, 50 per cent. of magnesia, and 6 per cent. of ferrous oxide; they may contain 80–90 per cent. of forsterite, but the accessory minerals present tend to lower the refractoriness so seriously that many natural olivines are useless unless "improved" by adding magnesia, which converts $MgO.SiO_2$ into $2MgO.SiO_2$ and ferric oxide into magnesio-ferrite. When a dunite is heated in an oxidising atmosphere it changes its colour from greyish-green to brown, as a result of the oxidation of the ferrous iron to $MgFe_2O_4$ or γ-Fe_2O_3, which is then seen to be segregated as brown translucent grains and flakes along the cleavage planes. The purest dunites occur in Norway.

The specific gravity (3·2–3·9) and the melting-point (1320°–1910° C.) vary with the purity, so that the importance of some of them as refractory

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[1] Birch and Harvey, *J. Amer. Cer. Soc.*, 1935, **18**, 176–192.

materials has been much exaggerated. Thus, the use of " natural olivine rock " (Eng. Pat. 283,791) without a close specification as to its composition and refractoriness is likely to lead to disappointment. The magnesium-iron olivines form a continuous series, with forsterite, Mg_2SiO_4, at one end and fayalite, Fe_2SiO_4, at the other; the melting-points of these extremes and of all intermediate mixtures are shown in fig. 34.[1] From this it is seen that an olivine crystal containing 85 per cent. of forsterite and 15 per cent. of fayalite will begin to melt at 1730° C. and will be completely fused at 1865° C.

Only two magnesium silicates are stable at high temperatures:

(i) forsterite, $2MgO.SiO_2$, m.-pt. 1910° C.;
(ii) clinoenstatite, $MgO.SiO_2$, m.-pt. 1562° C.

The latter is much less refractory and should be avoided when possible.

Artificial or Synthetic Olivine was first made by Berthier in 1823, by heating magnesia and silica in suitable proportions—nominally 57 parts of magnesia and 43 parts of silica, but a range of 35–65 and 70–30 respectively is sometimes used. German Pat. 417,360 claims that the use of a mixture of Epsom salts and quartz heated to 1500° C. produces olivine more cheaply than the use of magnesite. The use of 2 per cent. of alkali chlorides as a mineraliser in the magnesite-silica mixture was suggested by Reinhart in 1932. Refractory material consisting of merwinite (p. 235) and calcium orthosilicate is made by heating a mixture of lime, silica, and magnesia with or without a mineraliser. The product when crushed has hydraulic properties (Eng. Pat. 481,281—1936). For making synthetic olivines a catalyst is necessary; the impurities present in the raw materials usually serve this purpose, but sometimes boric oxide, calcium borate, or magnesium sulphate is used.

Instead of magnesite or magnesia a magnesian limestone or dolomite may be used in order to form *monticellite*, $CaMgSiO_4$, which is isomorphous with forsterite and is a member of the olivine series. It occurs too rarely to be used as a refractory material, and the synthetic product—obtained by fusing dolomite and sand—is scarcely known in commerce. H. A. Kennedy (U.S.A. Pat. 111,853) states that if more than 12 per cent. of silica is present in a dolomite, calcium orthosilicate is formed and is objectionable. In the same patent he advises the use of a little iron oxide to toughen the product.

The production and use of recrystallised olivine was patented in 1927 (Eng. Pats. 301,547, 307,391). The addition of chromium compounds, when preparing a synthetic olivine, was patented in 1934 (Eng. Pat. 441,516).

Various minerals, such as serpentine and steatite, are also used, their composition being " corrected " by the addition of magnesia; in that case care should be taken to avoid impurities which will unduly reduce the refractoriness.

When talc is heated alone, it does not form $3MgO.4SiO_2$ or forsterite, but clinoenstatite and cristobalite; the former is objectionable in refractory bricks.

Argillaceous talc and steatite when heated alone can form magnesia spinel, $MgO.Al_2O_3$, which can combine with silica on further heating and form cordierite, but this is too fusible to be of use. With all these minerals it is necessary to add magnesia to ensure the formation of forsterite.

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[1] Bowen and Schairer, *Amer. J. Sci.*, 1935, **27**, 151–217. See also Birch and Harvey, *J. Amer. Cer. Soc.*, 1935, **18**, 176–192.

Strictly, the mixture of the various materials should be fused and allowed to crystallise, for which treatment an electric furnace is to be preferred (see Eng. Pat. 20,378—1906). The addition of a little iron oxide prior to fusing was also patented in 1935 (Ger. Pat. 618,094). Other " mineralisers " include sodium silicate and various chlorides; about 2 per cent. of mineraliser is sufficient. If only silica and magnesia are used and the silica is in correct proportion or deficient only forsterite will be formed, but with an excess of silica (*i.e.* with insufficient magnesia) magnesium metasilicate is produced and is objectionable.

Where practicable, the use of silica and magnesia alone has obvious advantages, but considerations of cost have led to the extensive use of cheaper compounds of magnesium.

CORDIERITE SERIES.

Similar to the olivines are the products obtained by fusing mixtures of kaolin and magnesite; their refractoriness varies greatly according to the composition. With 32 per cent. of magnesia the refractoriness is only 1300° C., but with more than 50 per cent. of magnesia the refractoriness is 1710° C. or above. The typical mineral product is *cordierite,* $2MgO.2Al_2O_3.5SiO_2$, the α-form of which has a very low expansion.[1] The thermal expansion decreases with an increase in kaolin, and the tendency to spall also decreases.

Cordierite is a complex alumino-silicate corresponding to $4(Mg,Fe)O.4Al_2O_3.10SiO_2.H_2O$. The crystals are blue with a variety of yellow shades and belong to the orthorhombic system, though they occur chiefly as pseudo-hexagonal crystals. The specific gravity is 2·6–2·7 and the hardness 7–7·5. The refractoriness is that of Seger Cone 14 (1410° C.) and the coefficient of thermal expansion [2] between 0° and 1000° C. is $2{\cdot}48 \times 10^{-6}$.

The firing-range of cordierite is very short; it is said to be improved by the addition of 20–30 per cent. of zirconia.

Synthetic cordierite (without any combined water) can be made by heating in suitable proportions:

(*a*) talc, kaolin and corundum or anhydrous alumina;
(*b*) basic magnesium carbonate, flint and anhydrous alumina;
(*c*) forsterite and clay;
(*d*) forsterite, alumina and silica.

On heating above 1400° C. cordierite forms spinel and mullite. Unfortunately, the melting-point of cordierite and most of the allied minerals is too low for them to be regarded as refractory materials. A more refractory material is produced when a mixture of magnesia (or magnesite) and a pure clay is heated sufficiently to form mullite and free silica. The latter then combines with the magnesia and forms forsterite without seriously attacking the mullite. A brick of such a composition would have a melting-point of 1850° C., but like most products of magnesia, alumina and silica, it would have a low resistance to slags.

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[1] Cross and Rees, *Trans. Cer. Soc.*, 1934, **33**, 429.

[2] Geller and Insley, *Bur. Stand. J. Res.*, 1932, **9**, 1; Cross and Rees, *Trans. Cer. Soc.*, 1934, **33**, 379–442.

THE PYROXENES.

There are four crystal forms[1] of $MgSiO_3$: (*a*) monoclinic pyroxene, formed by maintaining the molten material a little below its melting-point (1521° C.) or by heating any form of $MgSiO_3$ to 1150°–1300° C., specific gravity 3·19; (*b*) orthorhombic pyroxene, formed at 1000°–1100° C., specific gravity 3·17; (*c*) amphibole, formed by rapidly cooling the molten material; (*d*) an orthorhombic amphibole formed by heating the molten material to above 1600° C. and cooling rapidly, specific gravity 2·85. The only form stable at all temperatures is the monoclinic pyroxene.

The pyroxenes are not sufficiently heat-resisting to be regarded as commercial refractory materials, but *merwinite* ($3CaO.MgO.2SiO_2$) may be regarded as a lime-magnesia pyroxene. It has been proposed for this purpose (Eng. Pat. 464,047), the material being used in either its natural or synthetic form.

THE SPINELS.

True spinel is magnesium aluminate, $MgO.Al_2O_3$ (French: *spinelle*), but the term " spinel " is applied to a large number of substances corresponding to the formula $R^{II}O.R_2^{III}O_3$ or $R_2^{III}(R^{II}O_4)$, so that the spinel group includes:

		Melting-point, ° C.
Spinel	$MgO.Al_2O_3$	2135
Zinc spinel (gehlenite)	$ZnO.Al_2O_3$	
Magnetite	$FeO.Fe_2O_3$	
Magnesium ferrite	$MgO.Fe_2O_3$	1770
Chromite	$FeO.Cr_2O_3$	
Chrysoberyl	$BeO.Al_2O_3$	
Pleonaste	$Al_2(Mg,Fe)O_4$	
Hercynite	Al_2FeO_4	
Picotite	$(Al,Cr)_2(Mg,Fe)O_4$	
Galmite	Al_2ZnO_4	
Franklinite	$Fe_2(Zn,Mn)O_4$	
Lime spinel	$CaO.Al_2O_3$	
Magnesium chromite	$MgO.Cr_2O_3$	2000[2]

The spinels are usually dark coloured or black, but some are red and others are green. All spinels crystallise with sharp edges (hence the name) in the cubic system and typically as octahedra. All spinels except magnetite are mixed oxides, and in some the composition is complicated by the partial replacement of one metal by another, as symbolised by the use of ordinary brackets ( ) above.

Magnesia spinel forms a series of solid solutions with alumina, which includes the following eutectics:—

Magnesia, per cent.	Alumina, per cent.	Melting-point, ° C.
45	55	2030
2	98	1925

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[1] Allen, Wright and Clement, *Amer. J. Sci.*, (4), 1906, **22**, 385.

[2] *Siemensite* is an artificial double spinel composed of magnesia, chromite and alumina (see p. 529).

The specific gravity of true spinel is about 3·6 and its hardness about 8. It has a very low coefficient of thermal expansion and so is very resistant to sudden changes in temperature.

True spinel is not attacked appreciably by basic fluxes and only slightly by acid slags. Molten metals do not attack it. The specific heat is 0·194.

Artificial spinels are usually made by heating a mixture of magnesia (dead-burned magnesite) with alumina (calcined bauxite or alunite) to temperatures exceeding 1650° C. and preferably to complete fusion. For the complete conversion to spinel it is necessary to fuse a mixture containing approximately 72 per cent. of alumina and to allow the spinel to crystallise.[1] A mineraliser may be added before heating so as to reduce the temperature required, but this also tends to produce a less refractory product. Chesters and Parmlee[2] have found that in mixtures of magnesia with alumina or chromic oxide the rate of spinel formation at 1500° C. is greatly increased by the addition of 2 per cent. of boric acid. Bauxite containing iron oxide should not be used as the reduced iron is objectionable. Experiments in Russia have shown that the electrical fusion of magnesia and clay and of magnesia and nepheline also produces refractory spinels, and that mixtures of magnesite and kaolin or cyanite do not produce spinels.

RARER REFRACTORY MATERIALS.

Rarer refractory oxides are used chiefly for experimental crucibles to be heated to the highest temperatures of the electric arc and under reducing conditions. They are too costly for more general use, notwithstanding the demand for materials having their properties for electrical and metallurgical furnaces.

The most important of the refractory rare oxides are—

Beryllium oxide (BeO)	melting at	2450° C.
Cerium oxide (CeO_2)	„	1950° C.
Lanthanum oxide (La_2O_3)	„	1840° C.
Tantalum pentoxide (Ta_2O_5)	„	1875° C.
Thorium dioxide or thoria (ThO_2)	„	2470° C.
Titanium oxide (TiO_2)	„	1350° C.
Yttrium oxide or yttria (Y_2O_3)	„	2400° C.
Zirconium oxide or zirconia (ZrO_2)	„	2720° C.

Beryllium oxide is obtained from beryllium ore or beryl, which occurs as an accessory mineral in granitic rocks in France, Rocky Mountains (Canada), Bellore (Madras), Kdarma (Bihar), Padyur (near Kangayam), Coimvatore (India), Emmaville (New South Wales), various localities in Western and South Australia, Tasmania, Madagascar, Black Hills of South Dakota, Maine, New Hampshire, Russia, Finland and (in small quantities) in Central Europe. The beryllium ore—which contains only about 15 per cent. of beryllia—is treated with sodium silico-fluoride at 850° C., and the resultant sodium fluoberyllate is dissolved in boiling water, filtered, and the beryllium oxide precipitated with caustic soda. Further purification can be effected by converting it into the sulphate, re-crystallising, and re-converting it into the oxide.

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[1] Rankin and Merwin, *J. Amer. Chem. Soc.*, 1916, **38**, 571.

[2] The use of boracic acid forms part of Eng. Pat. 2994, 1907. See also Chesters and Parmlee, *J. Amer. Cer. Soc.*, 1934, **13**, 51.

Beryl is a double silicate of beryllium and aluminium with the formula $3BeO.Al_2O_3.6SiO_2$, containing 10–14 per cent. of beryllium oxide and having a refractoriness of 1410°–1430° C. Other beryllium ores (with the percentage of the oxide in each) are *phenacite*, Be_2SiO_4 (44–46), *bertrandite*, $Be_4Si_2H_2O_9$ (40–43), and *hambergite*, $BeOH.BeBO_3$ (50–53). There are several other minerals, which contain less than 20 per cent. of beryllium oxide. The proportion of beryllium oxide in its best-known mineral, beryl, is only about 4 per cent. The separation of this oxide from its ores and from accessory minerals is very tedious and expensive, as it involves a fusion and several precipitations. Mixtures of beryllium oxide and kaolin containing more than 6 per cent. of the oxide have a refractoriness equal to Seger Cone 18 (1500° C.). Beryllium silicate (*phenacite*) is unstable. Beryllium oxide is soluble in water; it has an exceptionally high electrical resistance, a high thermal conductivity and an extraordinary resistance to sudden changes in temperature.

Beryllium oxide is very resistant to reducing agents, but it must not be brought into contact with other oxides as these greatly reduce its refractoriness. For the same reason, only very pure beryllium oxide can be used as a refractory material. It is very costly.

Beryllium oxide is used for special crucibles in experimental electrically heated furnaces, for protecting sheaths for thermo-couples under very trying conditions, and as a support for electrical resistance wires used at very high temperatures.

As a refractory material in the ceramic industry, beryllia is a weaker base than magnesia, and is more resistant to acids. W. P. Thomson (Eng. Pat. 2438 of 1915) uses a mixture of 100 parts of powdered beryllia to 1 part of colloidal beryllia, with about 0·1 per cent. of free acid for crucibles and other fireproof vessels.

Ceria occurs principally as *cerite*, which is a hydrated cerium silicate found in massive form or in granular deposits containing 59 to 72 per cent. of ceria and 1 to 7 per cent. of yttria. At Bastnäs, it is found in gneiss in association with mica, hornblende, allanite, and chalcopyrite. In Texas, Norway, Sweden, etc., it is also found as *allanite*, a basic orthosilicate of calcium, aluminium, iron, and cerium; as *monazite* (cerium orthophosphate), containing 60 to 70 per cent. of ceria, in Norway, Ceylon, North and South America, etc.; and as *æschenite* (cerium columbo-titanate), containing 15 to 24 per cent. of ceria.

Ceria, or cerium dioxide, is a very refractory compound, its melting-point exceeding 1900° C. It is very stable, and is highly resistant to acids and alkalies, except in the presence of a reducing agent. It also acts as a catalytic agent, and is used to the extent of 0·8 to 1·0 per cent. in gas-mantles. F. Wolf-Burckhardt and A. Borchers have suggested the addition of small quantities to silica glass.

Didymia is extracted from *cerite* and *monazite*. It is used to a very small extent in the gas-mantle industry.

Lanthanum is also extracted from *cerite* and *monazite*. The sesquioxide *lanthana* is a white powder having, according to Clève, a density of 6·53. It is soluble in acids and readily absorbs water. At present it is not used commercially as a refractory material.

Thoria is an oxide of thorium with the formula ThO_2. It occurs as *thorianite*, containing 70–80 per cent. of the oxide, and *thorite*, containing 48–72 per cent. Some monazite sands contain about 18 per cent. of thoria. It also occurs in small quantities in ultra-basic rocks. It is highly refractory (melting-point 2470° C.) with a specific gravity of 9·3–9·7, a coefficient of thermal expansion between 25° and 800° C. of $9{\cdot}3\times10^{-6}$ and a specific heat of 0·059. It is highly resistant to basic slags, but very sensitive to sudden changes in temperature. After calcination it is insoluble in acids.

Thoria is the principal material in incandescent gas-mantles, small proportions of ceria and beryllia being also present. W. P. Thomson (Eng. Pat. 2438 of 1915) claims the use of a mixture of powdered thoria and colloidal thoria in the proportions 100: 1, together with 0·1 per cent. of free acid, for refractory crucibles. E. Podszus (Eng. Pat. 11,771 of 1912) uses a similar mixture, and suggests the use of temporary bonds such as gelatin, gum, etc.

Thoria is used for making crucibles for experimental work at high temperatures, particularly for volatilisation *in vacuo* (see p. 594).

Titanium oxide occurs in nature in 36 different minerals, but it is obtained commercially only from rutile, ilmenite, and titaniferous magnetite. Rutile is the most important source of titanium oxide; it occurs principally in igneous rocks, pegmatite dykes, and metamorphosed rocks. In Virginia and Quebec (America) and in Southern Norway it is associated with gabbro; and in the first-named situation it also occurs in pegmatite dykes. It is also found to the north-east of Adelaide (South Australia), and in the sands and gravels of the Carolinas (U.S.A.). Ilmenite and titaniferous magnetite occur chiefly in igneous and basic metamorphic rocks, and also in pegmatites and veins usually associated with gabbros and eruptive rocks. The principal situations where they are found include: Rhode Island, New York, New Jersey, Virginia, North Carolina, Wyoming, Minnesota, Colorado, St Urbain (Canada), Ekersund (Norway), Routivare and Taberg (Sweden).

Anatase (sp. gr. 3·9) and brookite (sp. gr. 4·1–4·2) are converted into rutile (sp. gr. 4·0) on heating to 900° C., or to a lower temperature in the presence of a suitable mineraliser. Rutile is stable at high temperatures.

Pure titanium dioxide is obtained by fusing a titanium mineral with an alkali carbonate. The resulting titanate is dissolved in hydrochloric or sulphuric acid and the hydroxide is precipitated by adding ammonia. The hydroxide on calcination forms the oxide. An alternative method consists in dissolving the ore in sulphuric acid, diluting the product with water and heating carefully. Titanium hydroxide is precipitated, separated and afterwards calcined.

Commercially pure titanium oxide is used on a large scale in the manufacture of opaque white pigments and enamels. This is the most convenient form of titanium oxide for use as a refractory material.

Pure titanium dioxide melts at 1850° C.; rutile melts at 1815° C.; it has a hardness of 6 on Mohs' scale, a refractive index of 2·6 and a specific gravity of 3·9. In its chemical properties titanium dioxide resembles silica, but is more soluble in strong acids. Titanium dioxide forms no true compounds with silica, but a eutectic containing 10 per cent. of titanium oxide melts at 1550° C.

Titanium dioxide and alumina can combine, forming $TiO_2.Al_2O_3$ melting at 1860° C.; there are two eutectics—one containing 20 per cent. of titanium oxide and melting at 1715° C., and the other containing 38 per cent. of titanium oxide and melting at 1850° C.

When titanium oxide is fused with lime or calcium carbonate, the calcium titanates $3CaO.2TiO_2$ and $2CaO.3TiO_2$ are formed.

In a mixture of lime, alumina and silica heated to fusion Nishioka[1] found only one eutectic, containing 35 per cent. of $CaO.TiO_2$ and melting at 1530° C.

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[1] *Kinozuku-no-Kenkyu*, 1935, **12**, 537.

Mixtures of titanium oxide and magnesia become impermeable when heated to 1460° C., but the shrinkage is 26 per cent.[1] The refractoriness exceeds Seger Cone 27 (1610° C.). The eutectic between titanic oxide and zirconia melts at 1750° C. The shrinkage at 1460° diminishes with increasing zirconia content from 23–11 per cent. The heated mixture is impermeable when less than 20 per cent. of zirconia is present.[1] The dielectric losses are less than for other ceramic materials.[1] For the effect of titanium oxide on clays, see p. 96.

Titanium metal is chiefly used as a refractory material in incandescent electric lamps, but the oxide is used as a refractory colouring material, and has also been suggested for refractory bricks. W. P. Thomson (Eng. Pat. 2438 of 1915) uses 100 parts of powdered titanium oxide and 1 part of the oxide in a colloidal form, together with 0·1 per cent. of free acid, for making highly refractory crucibles. E. Podszus (Eng. Pat. 21,378 of 1914) has suggested the use of titanium nitride as a refractory material.

Yttria.—The chief yttrium minerals are *gadolinite*, *xenotime*, and *fergusonite*, of which gadolinite is by far the most important. It is a basic orthosilicate of yttrium, beryllium, and iron in the form of dark masses of crystals usually found in pegmatites and corresponding approximately to $FeO.2BeO.Y_2O_3.2SiO_2$, and containing 36 to 48 per cent. of yttria. It is quarried at Barringer Hill near Bluffton, Llano County, Texas. *Xenotime* is a form of yttrium orthophosphate which occurs in gneiss, granite, etc., in Scandinavia and North and South America, containing 54 to 64 per cent. of yttria. *Fergusonite* or yttrium metatantalate and columbate is found in Greenland, U.S.A., and Scandinavia; it contains 30 to 46 per cent. yttria. It also occurs as *yttrotantalite*, *samarskite*, *euxenite*, and *polycrase*, which contain lesser quantities of yttria.

Yttria is a white powder having a density of 4·84. It absorbs carbon dioxide and is readily soluble in acids. It is used to a small extent in the manufacture of Nernst lamps, the filaments being composed of a mixture of yttria, thoria, and zirconia.

Terbium and **erbium** are derived from yttrium, and have high melting-points, though they are too rare to be used on a commercial scale.

Cadmium Oxide has been patented by Pilling and Bedworth (U.S. Pat. 1,467,810) as a refractory material, either alone or mixed with powdered zircon. When heated to 800° C., it forms a compact mass of moderate tensile strength which is stable at high temperatures, and is useful for resistances for electric furnaces, furnace tubes, etc. Its resistivity is negative even at 1000° C.

Zirconia[2] (ZrO_2) is an oxide of the metal zirconium, and is best known as one of the constituents of mantles used for incandescent gas lighting; it has attracted considerable attention during recent years on account of its great refractoriness.

The chief source of zirconia is Brazil, where extensive deposits of baddeleyite have been discovered in association with a phonolite rock on an undulating plateau in the Caldas region, 130 miles north of São Paulo. In that locality, zirconia exists in three different states: (*a*) Pebbles found in the river-beds and on talus slopes; they vary in size from ½ inch to 3 inches in diameter, and have a specific gravity of 4·8 to 5·2. They contain about 90 to 93 per cent. of the zirconium oxide. (*b*) A greyish or bluish-black ore containing zirconium

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[1] Rieke and Ungewiss, *Ber. deut. ker. Ges.*, 1936, **17**, 237–264.

[2] It is interesting to note that before the first incandescent mantle (1885), zirconia was a rare and expensive material. Now it is available in such quantities that three firms are engaged in manufacturing zirconia crucibles. One British firm has used it for lining furnaces and another for making firebricks!

silicate (zircon) and zirconium oxide. (c) Black glassy pieces of almost pure zirconia. The light-coloured ore contains the equivalent of 73 per cent. of the oxide, whilst the darker varieties contain 80 to 85 per cent.—The ore has several large outcrops on the western side of the plateau, and is not difficult to work, as it is usually obtained by the aid of picks, crowbars, etc., blasting being employed in the case of large masses which cannot be broken by hand. As the work is done chiefly by native labour, the cost is very small, and the crude ore can be placed on the wagons at a low price. The masses are generally broken down to a suitable size, and are then roughly screened and washed to remove the clay and some of the iron and other impurities present. The product is then taken to the railway in very primitive carts drawn by twenty to thirty oxen, each cart holding about a ton of broken material. The roads are extremely bad and progress is slow, so that the output of a quarry is much less than it might be under more suitable conditions.

The following analyses reported by H. C. Meyer show the composition of various samples of the ore :—

TABLE LVII.—ANALYSES OF ZIRCONIA ORE.

	A.	B.	C.	D.	E.	F.
Zirconia	93·18	81·75	86·57	85·93	82·00	71·88
Silica	1·94	15·49	2·50	9·35	11·38	25·31
Titanium oxide . . .	0·69	0·50	1·43	1·84	0·36	0·63
Iron oxide	2·76	1·06	5·29	1·93	2·08	0·43
Alumina	0·64	0·85	1·00	0·36	0·62	0·15
Manganous oxide . .	trace	trace	..	..	..	..
Water . . .	0·47	0·63	3·32	1·56	3·35	1·56

Baddeleyite also occurs in the gem gravels at Rakwana, Ceylon, its colour varying from white to grey-brown, bluish-black, and dark green; it has a hardness of 6·5. A sample of Ceylonese baddeleyite analysed by G. S. Blake showed 99 per cent. of zirconium oxide.

Zirkite or *Brazilite* is a trade-name for a mixture of baddeleyite and zircon which contains 70–94 per cent. of zirconia and 1–25 per cent. of silica. It is very variable in composition and its properties are the same as those of a mixture of zirconia and zircon.

Zircon or zirconium silicate is a very widely distributed mineral (see p. 243). Zirconia can be manufactured from it by several methods, the most direct of which consists in heating it in an electric furnace, whereby the silica and most of the other impurities are volatilised.

Other sources of supply of zirconia minerals are : many of the states of the U.S.A., but particularly Florida, Montana, North Carolina, Virginia and Wisconsin, Canada, Mexico, the West Indies, the Gold Coast, Madagascar, Rhodesia, the Cape of Good Hope, the Transvaal, Ceylon, Travancore (India), Japan, Siam, Australia, Austria, Haute Loire (France), and the Ural Mountains (Russia).

Purification.—Crude zirconium ore is of little value compared with the pure oxide, and various methods have been suggested for purifying it in a sufficiently cheap manner. E. Wedekind has suggested boiling the crude mineral with sulphuric acid (which removes most of the iron and titanium oxides), the residue being treated with hydrofluoric and sulphuric acids, followed by ignition, to remove the silica.

A more satisfactory method for obtaining pure zirconia consists in fusing 5 parts of the crude ore with 15 parts of sodium carbonate and 25 parts of borax in a reverberatory furnace, the mixture being constantly stirred, and after about two hours, or when the reaction is complete, the material is cooled. It is finely ground and then lixiviated with water, the sodium zirconate passing into solution, leaving the iron, titanium, and other impurities behind as an insoluble residue. The solution is then filtered, concentrated, and allowed to crystallise, any silica (which is in the form of sodium silicate) being removed by passing carbon dioxide through the solution. Barium carbonate may be used in the same way as soda, the barium zirconate being extracted with hydrochloric acid and, after removing the silica by evaporation to dryness, the zirconia is taken up in the form of zirconium oxy-chloride, which crystallises out on concentration, and is afterwards taken up with water and precipitated with ammonia, the resultant product being very pure.

E. Wedekind has combined these two methods very successfully by first boiling with hydrochloric or sulphuric acid to remove most of the iron and titanium oxides, and then fusing the product with three times its weight of sodium carbonate and five times its weight of borax, stirring frequently. When cool, the mass is lixiviated with water and the filtered solution (which has a specific gravity of 1·16) is concentrated by the aid of steam in an iron boiler to a specific gravity 1·32 to 1·36, and is cooled and allowed to crystallise out.

A neater method consists in fusing the partially purified ore with acid sodium sulphate (nitre cake), and this has been used on a small commercial scale with complete success. By using one or other of these methods, there is now no serious difficulty in obtaining zirconia containing more than 99 per cent. of the pure oxide.

Zirconia occurs in four modifications:[1]

A—trigonal or pseudohexagonal-rhombic crystals, produced by prolonged heating of ZrO_2C to at least 1900° C.;

B—tetragonal crystals, stable at 1000°–1900° C., sp. gr. 6·10;

C—monoclinic crystals, stable below 1000° C., sp. gr. 5·56. Unit cell: a=5·21Å., b=5·26Å., and c=5·37Å.;

D—amorphous.

Baddeleyite (*C*) is the form stable at low temperatures, though *A* and *B* can also exist. The change from *C* to *A* or *B* is accompanied by a large contraction (10 per cent.) at 1000° C.

Pure zirconia has a melting-point of 2750° C., but commercial samples melt between 1700° C. and 2750° C. The specific gravity of crude zirconia is 4·0–5·8, but that of the purified and calcined zirconia is 5·4–6·0 according to the purity and temperature of calcination.

The hardness of the crystalline mineral is 6·5, but at 1500° C. zirconia is soft and easily yields to pressure, so that, in spite of its high melting-point, its refractoriness under a load of 50 lb. per sq. in. is only about 1340° C.

The specific heat between 25° C. and 1400° C. is 0·175.

The coefficient of thermal expansion depends on the temperature to which the zirconia has previously been heated. Material burned at 1250° C. has a coefficient of about $3{\cdot}8 \times 10^{-6}$, but that burned at a higher temperature has a coefficient of $6\text{–}8{\cdot}5 \times 10^{-6}$. The much smaller figures obtained some years ago appear to be much too low. The thermal and electrical conductivities are also low. The thermal conductivity of pure zirconia is 0·0036 g.-cal. per cm.^{3} per °C. per second.

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[1] Cohn and Talksdorf, *Zts. physikal. Chem.*, B, 1930, 8, 331.

The *shrinkage* of raw or precipitated zirconia when heated is so great that it is almost impossible to make articles of such zirconia on account of the excessive cracking which occurs. On cooling, the *B*-form tends to revert to the *A*-form, with more cracking. This inversion is prevented by the addition of 2–4 per cent. of magnesia to the zirconia before heating. In the absence of magnesia or other inhibitant, the shrinkage is progressive with the increase in temperature, as shown in the following figures:—

Temperature, ° C.	Linear Shrinkage, per cent.
1050	0·6
1100	0·8
1200	2·2
1300	4·5
1450	7·8
1500	9·5
1600	2·6
1850	0·2

After adequate heating at 1800° or above, so that it is fully shrunk, zirconia is not attacked by any acids except hydrofluoric acid, and only slightly by bases. The imperfectly shrunk material is less resistant. The electrical resistance of pure zirconia is 1250 ohms per c.c. at 1200° C. and 300 ohms at 1400° C. Pure zirconia is the only useful electrical insulator at 2000° C., but impurities seriously reduce this property and zircon has no useful electrical resistance above 1200° C.

Zirconia is almost completely insensitive to thermal shock and has a high mechanical strength at high temperatures. In furnaces lined with zirconia temperatures up to 3000° C. can be reached.

Zirconia is amphoteric like alumina; it resists both acids and bases up to 2000° C. by forming a protective skin.

Zirconia is very sensitive to the impurities ordinarily present in it. As little as 3 per cent. of clay reduces the melting-point from 2700° C. to 2100° C., and most binding agents have a similar action and are liable to cause cracking and excessive shrinkage. When zirconia is heated with silica, either as an impurity or as an added substance, zircon (m.-pt. 2560° C.) is formed and possibly a eutectic melting at 2300° C. If soda is also present, sodium zirconium silicate (m.-pt. 1477° C.) and sodium zirconate (m.-pt. 1500° C.). On cooling the molten complex, zirconia and zircon are the first to separate.

Carbon at 1400° C. and above reduces zirconia, forming zirconium carbide. With magnesia, zirconia forms a series of mixed crystals; no simple compound is formed; beryllium oxide has a similar effect. Both reduce the melting-point to about 1500° C.

Zirconia is sensitive to reducing gases at 500°–1600° C. and should be used only in an oxidising atmosphere.

Uses.—Prior to use as a refractory material, purified zirconia should be heated for some time at 1500° C. or above and then ground.[1]

The calcined zirconia is devoid of plasticity and requires the addition of a bond in order to produce a material which can be shaped. In its refined state it is usually too pure to be used alone on account of its porosity, and some other material, such as magnesia or thoria, must be added to give a sufficiently dense mass.

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[1] The use of zirconia which has been heated to 1800° C. or above was patented in 1925 (Eng. Pat. 246,480).

Zirconia minerals are chiefly employed as " special refractories " for high temperatures on account of their high fusing-point, low coefficient of expansion, and low thermal conductivity. They are used chiefly for the manufacture of crucibles, capsules, and other small laboratory-testing apparatus, and also as bricks and blocks in industrial furnaces working at exceptionally high temperatures. Zirconia has also been employed for sparking plugs, high temperature insulators, etc. The manufacture of bricks and crucibles of zirconia, fused zirconia, and zircon will be found in Chapters IV. and XII. respectively.

Zirconia is sometimes used to coat or replace the lime or magnesia pencils in lime- and Drummond-lights, and in Blériot lamps a rod of zirconia is heated in a blow-pipe flame fed by oil and oxygen.

Colloidal Zirconia is used as a bond in the manufacture of articles made of zirconia. It may be made by extremely fine grinding followed by the use of a colloidal mill, or by diluting a solution of zirconium nitrate with 80 times its weight of water and dialysing. The latter is a very extravagant process, as only one-third of the zirconia becomes colloidal.

Fused zirconia is sometimes employed for the manufacture of small refractory articles owing to the fragility of the raw oxide and the difficulty of securing a suitable bond which will not impair the refractoriness of the article. E. Podszus has obtained this material by embedding a carbon electrode in coarsely ground calcined zirconia and heating the latter with the arc formed from a second carbon electrode, thus partially melting the zirconia with the formation of some carbide. The latter then acts as an electrode, and the zirconia fuses and continues to do so when the upper carbon electrode is slowly withdrawn. After a time, the arc becomes quiet, and the fusion proceeds rapidly. Arcs 12 inches long, accompanied by a molten mass of zirconia 6 inches diameter, have repeatedly been obtained in half an hour with a current of 50 amps. at 220 volts, the resulting blocks of zirconia being perfectly pure and white, with a yellowish sheen in parts due to traces of iron. The fused zirconia is ground for 100 hours or more in a steel ball mill, and any iron from the latter is removed by treating the powder with acid.

Instead of fusing the zirconia alone it may be mixed with alumina, lime, magnesia, or silica, and the mixture fused and allowed to crystallise; this reduces cracking by minimising the inversion of the zirconia (Eng. Pat. 429,367—1932).

Zircon ($ZrSiO_4$) occurs in relatively large quantities in North Carolina and Florida (U.S.A.), Brazil, Madagascar, and Southern Norway. It is generally in association with pegmatites and syenites, being found embedded in quartz, felspar, and riebeckite, or else in the massive form. It occasionally occurs as a result of metamorphism. Zircon sands occur in various parts of the United States, whilst monazite sands (from which zircon is obtained as a by-product) are found at Travancore (India), Brazil, and Florida.

Zircon, when pure, contains about 67 per cent. of zirconia and 33 per cent. of silica, though usually iron occurs to a small extent as an impurity. It crystallises in characteristic tetragonal crystals, the most common form being that of a prism with a pyramid at each end. The pure zircon is colourless, but the crystals are usually brown or yellow, on account of iron compounds present as impurities, though all shades through yellow, grey, green, and red also occur. It has a hardness of 7 to 8 and a specific gravity of 4·0 to 4·7. It is almost infusible, its melting-point being almost 2550° C.[1]

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[1] A more recent determination shows 2430° C., but no accurate figure can be found, as zircon decomposes just below or at its melting-point, the silica volatilising and leaving a residue of zirconia.

The linear expansion of pure zircon is 4·6 per cent.

Zircon forms two eutectics with silica, one (containing 97 per cent. of silica) melts at 1750° C., and the other (with 40 per cent. of silica) at 2220° C.

Zircon sand consists of tiny, colourless grains, similar to sea-sand, and contains about 64 per cent. of zirconium oxide. The crystals may be separated from most other minerals in which it occurs by electrostatic methods—the zircon grains being attracted to the electronegatively charged part of the machine, whilst most of the other minerals—being poor conductors—remain unaltered. The purified material is crushed and then mixed with 3 to 4 per cent. of chalk or 5 to 8 per cent. of china clay, and made into articles.

Zircon has the advantage of having no shrinkage when heated to 1750° C., and it is not affected by molten glass, slag, etc. The presence of a small amount of impurity in zircon is not of great importance in most cases. Zircon appears to be free from the tendency to form a carbide at high temperatures in the presence of carbon monoxide, which has proved objectionable in the case of zirconia.

The mineral is of special value in steel and electric furnaces, glassworks, etc., it having properties similar to zirconia, but requiring no chemical treatment in order to purify it before use.

REFRACTORY ELEMENTS.

The following are the principal refractory elements :—

Boron is a hard, black, amorphous non-metal, with a conchoidal fracture and a specific gravity of 2·34. It melts, according to Tiede and Birnbräuer, at 2200° C., but Weintraub gives 2800° C. as its melting-point. It has a low electrical conductivity, but becomes more conductive on heating. It may be heated in air without appreciable oxidation. It is a powerful reducing agent, many metallic oxides and salts being rapidly reduced by it.

Cast iron is refractory in the sense that it will resist high temperatures for a short time, and is much used in the chemical industry in the form of pans and crucibles.

Molybdenum is a very refractory metal, having a melting-point of about 2550° C. and a specific gravity of about 9·0, which is used chiefly in the electric lamp industry. It has no other important use as a refractory material.

Nickel is capable of withstanding 1400° C. for a considerable time, and is chiefly used in the form of small crucibles for laboratory purposes.

Osmium has a melting-point of about 2700° C., and is used in electric lamp filaments, usually as a coating over some other metal, such as platinum.

Platinum has a melting-point of about 1755° C., but it cannot be used constantly at temperatures much above 1300° C. to 1400° C. Its principal uses are for laboratory crucibles and for resistance wire at high temperatures. On account of its high cost its uses are very limited.

Tantalum is a tough white metal, having a high specific gravity (16·8). It has a melting-point of about 1800° C., and it is principally used for electric lamp filaments, and has the disadvantage of being readily oxidised and of absorbing hydrogen and nitrogen at red heat.

Thorium, which is obtained from various minerals found in nature, has a high melting-point (1700° C.), but it is not used to any great extent as a refractory material in the metallic state, though some is used in incandescent electric glow lamps both alone and in combination with tungsten.

Colloidal thorium is used as a binder for thorium and tungsten-thorium filaments.

Titanium is a hard, brittle, silver-white metal, having a specific gravity of about 4·8. Though it has a high melting-point (1800° C.), it is not largely used in the metallic state, as it readily combines with oxygen and nitrogen when heated. It has been used to a small extent for electric lamp filaments.

Tungsten is a white, brittle, crystalline metal, having a specific gravity of 16·17 and a hardness greater than glass. It is sometimes used as a refractory material, as it has an extremely high melting-point (about 3400° C.), and is also used in the form of crucibles, and in electric lamps as filaments. It has the advantage of not being attacked by lead at high temperatures, so that it may be used for lead baths in experimental work. It also has an enormous tensile strength, and is non-magnetic. It has been suggested as a possible material for glass pots, and Keyes has employed a carbon crucible lined with tungsten for the manufacture of silica glass.

Uranium (m.p. 1850° C.) in the metallic form is not used to any great extent as a refractory material. It has been suggested for the electrodes of arc lamps for the production of ultra-violet rays, and the salts of this metal are used in the ceramic industry as refractory colouring agents in glazes.

Vanadium has not, as yet, been employed as a refractory material, though it has a very high melting-point (about 1800° C.). It combines readily with carbon to form the carbide which has been used in electric lamp filaments.

Zirconium is not a very refractory metal (m.p. 1300° C.), and there are many difficulties connected with its use, as it is very difficult to reduce from the oxide, and is easily oxidised as well as readily combining with nitrogen, carbon, silicon, etc. It has been used to a small extent in the filaments of incandescent electric lamps, but otherwise it is little used. The oxide of zirconium is very useful as a refractory material.

On account of the difficulty experienced in obtaining sufficiently large quantities of most of these metals in a suitable condition, they have not been used extensively as refractory materials except in the electric lamp industry and for small laboratory apparatus.

REFRACTORY ALLOYS.

In addition to the *refractory metals* just mentioned, various heat-resisting steels and other alloys are available. They are not as refractory as most of the substances mentioned in this volume, but they have sufficient heat-resistance to justify their being mentioned here. Most of these refractory alloys are varieties of steel; some of them can be used continuously for long periods at any temperature up to 900° C. and for short periods up to 1000° C. One alloy of nickel and chromium is claimed by the makers to be able definitely to withstand temperatures up to 1100° C. for periods of long duration without damage. Its melting-point is 1420° C.—slightly lower than that of nickel. Other alloys can be used at temperatures not exceeding 1150° C. for short periods. The difference between the melting-point and the maximum temperature at which these alloys can be used is very large; it is chiefly due to the fact that the tensile strength of these alloys falls rapidly after the temperature has increased above 850°–900° C.

The best heat-resisting alloys contain 15–30 per cent. of chromium and 12–80 per cent. of nickel, with a small proportion of carbon in the case of heat-resisting steels. The proportion of chromium and nickel must be varied according to the user's requirements. An increase in the chromium and a decrease in the nickel (and in the tungsten, if present) increases the heat-resistance of the alloy, but may bring about other, undesirable properties, such as difficulty in machining. Very small differences in the composition of the alloys also have a marked effect on their behaviour. In other words, it is very difficult to obtain all the desired properties in one alloy and a compromise must usually be made for all temperatures above 850° C.

Refractory mixtures containing finely powdered metal or pellets of metal have been patented (see Eng. Pats. 184,887, 185,435, 197,340). In some cases, the metals specified are so easily oxidised that the use of such products seems to be of doubtful benefit.

The chief properties required in refractory metals and alloys are:

(i) Resistance to scaling; destruction by oxidation (scaling) is very liable to occur with some alloys. It is less likely when the metal is in contact with reducing gases than with air, so that a given alloy can usually be employed with a higher gas-temperature than air-temperature.

(ii) Inertness to products of combustion. All nickel alloys are liable to attack by sulphur in the furnace gases, and as Ni_2S has a melting-point of only 644° C. its formation destroys the heat-resistance of the alloy.

(iii) Stability under repeated heating and cooling or under prolonged heating (as required).

(iv) Adequate mechanical strength at the highest temperature attained in use. Heat-resisting alloys lose strength rapidly as the temperature rises above 800° C., but some retain sufficient tensile strength to be used at 900°–1200° C.

Most heat-resisting alloys are sold under proprietary names. They are made by the leading steel manufacturers and by other firms.

Refractory alloys are used for crucibles, carburising pots, pyrometer sheaths, retorts, chains for conveyors travelling through furnaces, recuperator tubes, muffles, fire-boxes, and for a variety of furnace fittings. They are also used extensively in foundries for heating various metals.

The following brief bibliography is useful—enquiries should also be made of the leading steel manufacturers: J. F. Kayser, *Trans. Cer. Soc.*, 1933, **32,** 381; Sarjant and Middleham, *J. Soc. Glass Tech.*, 1936, **20,** 685; Elliot, Sarjant, and Cullen, *Chem. Ind.*, 1932, **51,** 502; Hadfield, Elliot, and Sarjant, *J. Soc. Chem. Ind.*, 1930, **49,** 41 T.

SUNDRY REFRACTORY MATERIALS.

Concrete is not a satisfactory refractory material; it is decomposed at 120° C., especially in the presence of acid vapours. Although sometimes used, it should not be employed at high temperatures, as it is too unreliable. The use of a concrete composed of grog or other suitable non-plastic refractory material mixed with *ciment fondu* (Lafarge) is much more satisfactory. It is largely used as a refractory cement (see p. 746).

Steatite, Talc, and Soapstone are varieties of a compact cryptocrystalline hydrated magnesium silicate corresponding to the formula $3MgO.4SiO_2.2H_2O$, with a specific gravity of 2·7–2·9 and a hardness of 1 on Mohs' scale. It decomposes and melts incongruently at 1547° C., but impure talc is much more fusible.

Steatite, talc, and soapstone are essentially the same mineral in different states of aggregation. The purer varieties with a fibrous or leafy structure are called talc, whilst the massive varieties are known as steatite or soapstone. Some varieties of light-coloured mica are erroneously known as talc.

Steatite, talc, and soapstone, when heated at 840°–900° C., decompose into enstatite and amorphous silica, which, in turn, form clinoenstatite and cristobalite at high temperatures. According to Thilo, however, the product consists chiefly of a magnesium metasilicate (*metatalc* or *protoenstatite*), which is also produced on heating magnesia and silica, in suitable proportions, at 1300°–1400° C.

These materials are not suitable for use as a refractory material except at relatively low temperatures, though steatite is extensively used in the manufacture of refractory porcelain (p. 715), and slabs of it have been used for lining furnaces and stoves. Mixtures of steatite and magnesia have been made into magnesite bricks of good quality (see " Olivine Bricks," p. 462), because on heating magnesia and steatite in suitable proportions to 1450°–1500° C. forsterite is produced.

The addition of a small proportion of steatite to saggar clays greatly increases their durability.

Serpentine is an ultra-basic rock of very variable composition, but corresponding essentially to $3RO.2SiO_2.2H_2O$. Its average specific gravity is 2·5–2·6 and its hardness 3–4. As the name is applied to a group rather than to a single mineral, serpentine is not satisfactory as a refractory material, though it has been used for lining furnaces. It is a common impurity in magnesite and chromite.

Serpentine, when pure, has the composition $3MgO.2SiO_2.2H_2O$; it dissociates at 650° C. into forsterite, free silica, and water. On still further heating, the silica and part of the forsterite combine and form clinoenstatite, which melts at 1562° C. Impure serpentine melts much more readily. Any iron compounds present in it tend on heating to form fayalite.

To make a useful refractory material from serpentine it would be necessary to add magnesia to combine with the more fusible compounds and form forsterite. Even then, a serpentine brick will permit a considerable amount of fluid material to drain out of it if the brick is maintained at 1450° C. for several hours. According to L. Pieper[1] it is necessary to add sufficient magnesite to convert all the iron present into magnesioferrite, $MgO.Fe_2O_3$, and to combine with all the free silica so as to form forsterite, $2MgO.SiO_2$. For use as a refractory material serpentine should not contain more than 10 per cent. of iron oxide (reckoned as ferrous oxide).

Pudding stone is a conglomerate of pieces of rock cemented together with a natural bond. The pudding stone used for furnace linings is composed of pieces of quartz embedded in a siliceous matrix, roughly chipped into the form of blocks. Unfortunately, these blocks are much less reliable than silica bricks.

[1] *Ber. deut. ker. Ges.*, 1937, **18**, 42.

CHAPTER II.

THE MANUFACTURE OF FIREBRICKS FROM CLAY.

Common firebricks are the ordinary commercial fireclay bricks. The term has no relation to quality, but indicates that these bricks are more commonly used than any other kind of firebricks. They are used for all purposes where the heating conditions are not severe enough to necessitate a special kind of firebrick being used.

Firebricks to which no adjective is applied may be made of any refractory material which is suitable for the purpose. There are several different methods of manufacture and a wide choice of materials, though three-quarters of the firebricks in use are made of either fireclay or silica. In the present chapter only fireclay bricks are considered.

Uses.—Firebricks (fig. 35) made of clay are chiefly used in the construction of kilns, furnaces, ovens, fireplaces, flues, boiler settings, and other structures in which heat is generated, or through which hot gases pass (see Chapter XVIII.). Such bricks must, therefore, be able to withstand both a high temperature and the action of fuel, flue-dust, slags, and other corrosive materials. In many cases, fireclay bricks must not be adversely affected by sudden and great changes in temperature, and they must be sufficiently strong to support a reasonable load and to resist the required pressure when heated to the highest temperature to which they may be subjected when in use. They must not shrink so much as to endanger the safety of the structure in which they are employed.

Fireclay bricks which are able to satisfy all the foregoing conditions are exceedingly difficult to produce; it is much easier to manufacture bricks which will serve efficiently for the requirements of the less exacting users. Moreover, the cost of the firebricks is often so serious a consideration that most users must select the properties they consider most important for their special purposes, and must relinquish—or at least must not insist too strongly on—those which are of minor importance to them. At the same time, they should remember that " cheap " firebricks often lead to costly disasters.

Materials.—The chief materials used in the manufacture of clay firebricks are the fireclays of the Coal Measures (Chapter I.)—either raw or in the form of grog; a moderate quantity of firebricks is also made from china clay and kaolin wastes. On the Continent, the kaolin used is so slightly plastic that it is employed instead of grog; but in England the china clay, if used at all, is employed as a binding material.

China clay firebricks are made exclusively in Cornwall and Devon, those of Calstock and Lee Moor being the best known. Two parts of the washed sand from the china-clay pits are mixed with one part of the residue in the mica drags. The latter consists of a mixture of coarse china clay and sand, and is of a moderately plastic nature. The mixture is passed through a trough mixer or pug mill, in which it is well mixed with water, and the paste is moulded by hand and burned in round down-draught kilns with a capacity of about 16,000 bricks, in a similar manner to fireclay bricks (see *later*).

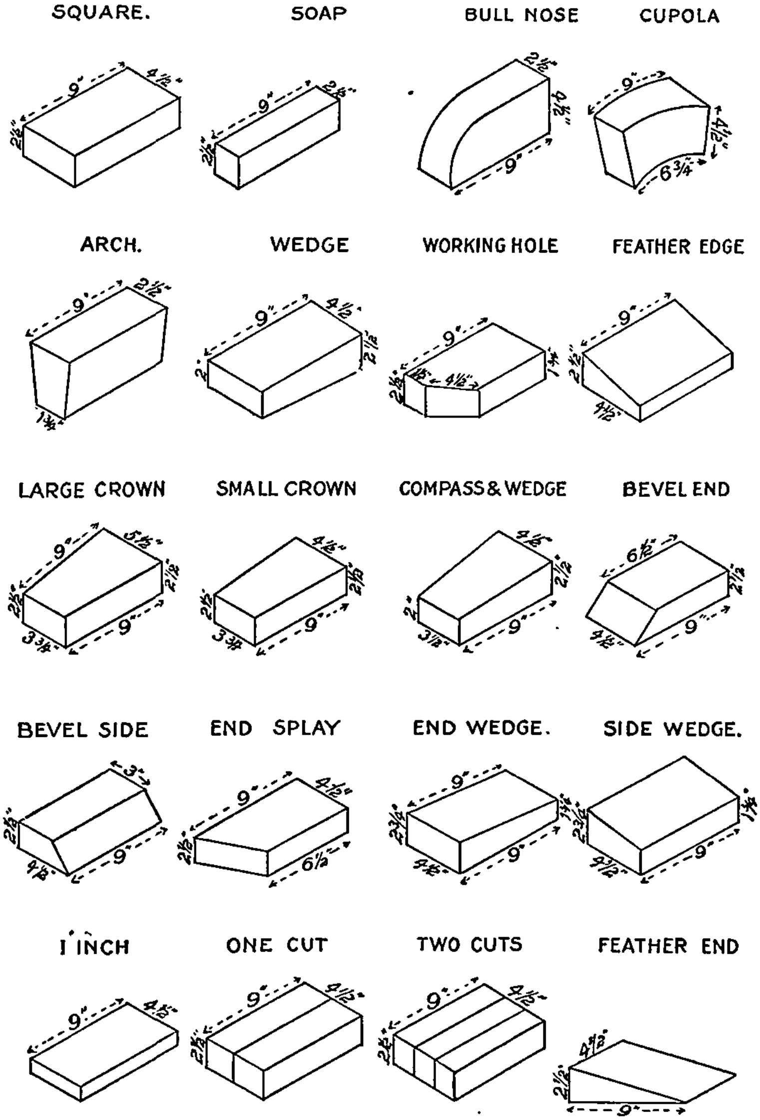

FIG. 35.—Various types of firebricks.

The bricks are seldom above No. 2 grade in quality, as the granitic sand of which they are composed is by no means devoid of fluxes. The best bricks made in this manner are, however, very strong and highly resistant to the cutting action of flue gases, so that they serve a useful purpose where a firebrick of moderate refractoriness but great mechanical strength is required. It should be noted that the bricks are not made of china clay alone, but of the waste material obtained in removing china clay from the rock in which it occurs.

Several patents have been granted for making china clay waste (free from clay) into bricks. The bond suggested is usually water-glass, tar, or Portland cement, none of which is wholly satisfactory. The great drawback to the use of this waste is its unfavourable location.

Bricks made of pure china clay are very occasionally made for use in experimental furnaces, for which purposes their purity and high refractoriness make them invaluable; they are too costly for use on a large scale. The Carbis China Clay Co. manufacture fireclay bricks from a siliceous china clay, the analysis of which is given on p. 27.

It is interesting to note that, in 1879, H. Bull patented the manufacture of refractory bricks, with a high resistance to acids, from china clay mixed with 10 per cent. of lime as bond. To most readers the addition of so much lime would appear to destroy the very refractoriness which makes china clay so much more valuable than other clays.

Fireclay bricks are chiefly made from the fireclays of the Coal Measures (Chapter I.). These Measures are so well known that during the past twenty-five years no new beds of fireclay of a quality better than formerly used have been discovered. These clays all have their well-defined limits of refractoriness, and the manufacturer has, therefore, to meet new conditions with fresh mixtures of known clays in various proportions; with suitable additions of calcined clay (grog) or other non-plastic material; by grinding to various degrees of fineness; by burning to various degrees of hardness; and by special treatment of the clays.

The foundation of a good brick lies in the clay, for it is wellnigh impossible to make a high-class firebrick out of unsuitable clay. Yet much may be done, even with an inferior clay, by careful and intelligent manipulation, and those who are fortunate in possessing a good fireclay should make no excuse for loose and careless methods, resulting in the production of an indifferent quality of bricks, but should use every effort to produce the highest grade of bricks possible. The first and principal requirement in a firebrick is that it shall be sufficiently durable;[1] in fact, it is quite useless without this quality, which depends on the chemical composition and on the physical properties of the bricks. According to the purposes for which the bricks are required, either a vitrifiable or a non-vitrifiable fireclay may be used.

Vitrifiable fireclays are those which attain a maximum contraction and become impervious to water at a relatively low temperature (say Cone 18, or 1500° C.) and yet a cone made of them retains its shape at Cone 28. Such clays make useful firebricks notwithstanding their long range of vitrification and their high content of fluxes (5–8 per cent.).

Non-vitrifiable fireclays contain too little fluxes to show an appreciable amount of vitrification at a temperature much below that corresponding to their refractoriness. In such clays the maximum contraction varies with the temperature attained. A subsequent heating at that temperature is accom-

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[1] It would be an error to substitute the word *refractory* for "durable" in this sentence. Refractoriness is merely resistance to heat alone; durability may demand resistance to slags, flame, gases, blows, changes of temperature, etc., in addition to refractoriness.

panied by a slight expansion and a slight disintegration of the mass, which results in a loss of strength. A subsequent heating at a higher temperature is followed by a further contraction, which attains a maximum as before. The non-vitrifiable fireclays are used where the conditions are most severe; the vitrifiable ones are used where resistance to abrasion and attack by flue-dust, slags, or other corrosive agents is more important than resistance to " heat."

The chemical composition and the properties of the various fireclays have been described in Chapter I., and from the information given there and in Chapter XVIII. it should not be difficult to select one or more clays suitable for the manufacture of any desired kind of firebrick.

In selecting clays for firebricks of the best class, it is desirable to start with a base of fireclay chiefly noted for its refractory or heat-resisting power. That is to say, the main portion of the mixture used should consist of a fireclay which may be lean or plastic, but whose chief characteristic is an exceedingly high temperature of fusion.

It should be observed that for many purposes firebricks must be made of two or more clays mixed together so as to secure a mixture which will have the requisite properties. The lack of plasticity of some fireclays must be counterbalanced by the addition of a more plastic clay. This binding clay need not be so refractory as the grog, as this might prevent it from exercising its full binding power, but it must be of such a nature that it will not devitrify on firing a number of times, dependent on the nature of the work which the bricks containing it are expected to perform. The excessive shrinkage of one clay must be overcome by the addition of a leaner clay, or of grog. The proportions of each of the clays must of necessity be left to each individual manufacturer, as they will depend on the particular clays he uses and on the requirements of the purchasers of his bricks. Herein lies one of the greatest difficulties in clayworking.

It is easy to find that the addition of certain clays to a mixture will produce an improved quality of bricks, but it is often extremely difficult to ascertain the cause of this improvement, more especially as a larger proportion of the same added clay may result in a worse brick than that formerly made. The blending of clays for this purpose is, in fact, one of the least understood of all the various departments of clayworking, and he is indeed a fortunate man who has been able (by whatever means) to produce a really successful blend of clays at a reasonable price. In carrying out attempts at securing a satisfactory blending of various clays, the greatest care should be taken to keep full and accurate records of what is done, as it not infrequently happens that experiments which at the time seemed complete failures prove later of great value, if full records have been kept.

In addition to fireclay it is also desirable to use a certain amount of grog, in order to provide a non-plastic material which will keep the shrinkage of the clay paste within convenient limits. The following table, due to W. C. Hancock, shows the decrease in shrinkage on adding grog to a plastic Stourbridge fireclay :—

TABLE LVIII.—EFFECT OF GROG ON SHRINKAGE OF FIRECLAY.

Mixture.		Grog Size.	Shrinkage. Per Cent.	
Clay.	Grog.		Air.	Fire.
100	0	$\frac{1}{8}$–$\frac{1}{16}$ in.	5·25	8·20
90	10	,,	4·47	7·25
80	20	,,	3·33	5·46
70	30	,,	3·08	4·17
80	20	$\frac{1}{16}$–$\frac{1}{30}$ in.	3·93	6·05
60	40	,,	3·24	3·97

Various kinds of grog may be used, including broken bricks, calcined clay, and bauxite. If broken bricks are used, care must be taken not to introduce too much glazed ware, as the glaze acts as a flux and tends to vitrify the ware. Burned clay should not be allowed to become mixed with coal or ashes, as these only make it impure. On this account, it is best to burn it in a down-draught muffle kiln in the shape of bricks. It is important that the grog should be at least as refractory as the clays used in an unfired state, or partial vitrification will occur, and the chief value of the grog as a skeleton-forming material will be lost. If the grog is not more refractory than the clay used to bind it, the mixture will crack sooner or later owing to the strains set up and the amount of sintering which takes place. This cracking may not occur at the first time of using, but will develop more or less rapidly on repeated heatings.

When it can be obtained sufficiently pure, and especially when the clay is somewhat poor in alumina, the substitution of burned bauxite for burned clay is a great advantage, because the fluxes present in the clay naturally reduce its refractoriness very seriously, but by adding to the clay a material of still higher heat-resisting power than the clay itself, it is often possible for the average refractoriness of the brick to be raised in spite of the fluxes present.

Bauxite should always be made into rough bricks and burned before use, as when raw bauxite is heated it evolves a large proportion of water and shrinks excessively. Calcined bauxite may be regarded as ordinary grog and treated in exactly the same manner.

The proportions of burned clay or bauxite to be added to the raw clay will depend on the plasticity and contraction of the latter. A strong clay will allow of the addition of a much larger proportion than will a less plastic clay. Hence, no definite proportions can be given, though four parts of raw clay and one part of burned material is frequently used, and some very plastic clays will stand the addition of an equal weight of burned material, and still enable the workmen to finish the surface properly.

It is in the proportion of grog used, and in the variations necessary in the method of mixing it, that the chief differences between German and British fireclay bricks are to be found. In Britain, it is customary to use fireclay as the chief constituent of the bricks and to add only sufficient grog to keep the shrinkage of the clay within convenient limits. For kiln floor blocks, arch blocks, etc., 80 per cent. of clay and 20 per cent. of grog is very satisfactory. Some plastic clays of fair refractory quality have a shrinkage as high as 1½ inches per linear foot. The addition of 20 per cent. of grog will reduce this to about 1¼ inches. For slightly better ware, such as cement kiln blocks, a mixture of 40 per cent. of clay, 40 per cent. of flint, and 20 per cent. of grog may be employed. This has a shrinkage of about 1 inch per linear foot. More refractory mixtures involve the use of a more plastic clay or grog. A high quality mixture having a shrinkage of ¾ to ½ inch per linear foot consists of 50 to 60 per cent. of hard clay, 15 to 25 per cent. of plastic clay, and 25 per cent. of grog. Where the minimum variation in dimensions and the maximum freedom from warping are desired, as much as 90 per cent. of grog is sometimes used, as such a mixture has scarcely any shrinkage.

In Germany, the grog forms the chief constituent,[1] and only sufficient plastic clay is used to bind the particles of grog together. British fireclays will not stand the addition of more than 30 per cent. of grog without becoming too " short " or low in plasticity to be used ; in Germany much more plastic binding clays are used, and only about 30 per cent. of raw clay is present in the German mixtures.

Silica is useful within certain narrow limits as a non-plastic or opening material, but it should not be employed more than is really necessary, its place being far more satisfactorily taken by grog made of clay or bauxite.

It is a common, but unfortunate, mistake to suppose that the addition of *silica* to fireclay improves the quality of bricks. This can only be the case where the clay is not sufficiently refractory to be termed a fireclay, and where the proportion of silica added is very large. Seger has shown experimentally that the addition of silica to a high-grade fireclay reduces the refractoriness of the clay, and, in addition to this, silica also shortens the range of vitrification. The only manner in which the addition of silica can truly be said to improve a fireclay is when bricks are desired which shall have a very small amount of shrinkage and be capable of resisting sudden changes in temperature without " shattering." In such cases the silica acts like grog ; but though it is much cheaper than grog, it is by no means so satisfactory. Such bricks are known as *semi-silica bricks* (see *later*).

Felspar is seldom or never added to a highly refractory clay as grog, but when used its effect is threefold. Below the temperature at which the felspar begins to soften, the shrinkage of the clay is reduced in the same manner as if grog had been added. At 1100° C. (in some cases at a rather higher temperature) the felspar and other fluxes begin to melt and to fill some of the pores in the material, so that the total porosity is reduced, but the shrinkage is not appreciably affected. If the percentage of felspar is sufficiently large, the softening-point of the clay is lowered and loss of shape may occur at some temperature above 1350° C., corresponding to the proportion of eutectic material present and to the load or pressure on the material. Simonis has shown that the addition of 30 per cent. of felspar to kaolin only reduced the refractoriness from Cone 35 to Cone 31, but under a load, loss of shape occurs at Cone 17.

Bauxite is sometimes mixed with fireclay in order to increase the refractoriness of the latter. Such mixtures are seldom satisfactory if the conditions of use are sufficiently severe to justify their use.

Various other additions have been suggested but are not of any particular importance. J. Bach, in 1905 (Eng. Pat. 7599), suggested the addition of aluminium hydrate and chromite to the fireclay.

T. Ward (Eng. Pat. 20,640 of 1905) adds plaster of Paris and finely divided cork in order to give a porous block. W. R. Carr and J. Urwin (Eng. Pat. 11,696 of 1905) suggest the addition of about 25 per cent. of coke or coke breeze; whilst R. Halkett (Eng. Pat. 103,232 of 1916) adds 1 part each of

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[1] These bricks are described later under the heading " Grog Bricks."

alumina, sawdust, and sodium silicate (1 part of sodium silicate to 2 parts of water) to each 15 parts of fireclay.

Carborundum is a useful grog, especially, according to M. F. Peters, where resistance to spalling and abrasion is required ; it also increases the resistance to deformation at high temperatures. It is too costly, however, to be used to any great extent.

Whichever method of manufacture is employed, the raw materials must first be brought into a suitable condition, so that they can be mixed together in the desired proportions. The methods by which this is effected comprise the following :—

Preliminary Sorting in Mine.—Fireclays are usually found at a considerable distance below the surface of the ground, and must, therefore, be mined in a manner similar to that used for getting coal. In fact, coal and fireclay are often obtained from the same pit, the fireclay being found beneath the coal.

The clays occur in various strata in close proximity to each other, but each having different composition and properties. Now, if all the seams were mined together the indiscriminate mixing of the various seams in unknown quantities could not be expected to give such reliable results as where each particular seam is mined separately, and definite proportions of each employed so as to ensure a combination of the best qualities. Great care, therefore, needs to be displayed in the separation by the miners, as unless suitable clays are supplied to the makers it is impossible to produce satisfactory bricks.

Having ascertained which are the best portions of the seam, these should be removed, care being taken that no shale, coal, or other foreign matter is included. The pit-wagons ("boxes" or "corves") used for receiving and conveying the clay should be kept for that purpose *only*, and the men employed in "getting" should likewise be restricted to that work, as they become experienced in discerning the materials which it is expedient to leave out.

Sorting.—The fireclay which has been raised to the surface by means of a shaft and lifting gear is taken thence to large sorting beds, where it is broken up and "selected" or "picked over" by experienced clay-sorters, who should endeavour to remove all iron nodules, shale, and other impurities.

Each kind or quality of clay should be kept separate and duly tested, so as to ascertain its nature as accurately as possible. This testing—notwithstanding its importance—is neglected in many works, yet it is apparent that if the characteristics of the clays used are not sufficiently known it will be difficult to rely on making satisfactory bricks.

The clay should always be sorted before being weathered, and for the best grades of bricks it should be sorted again after weathering. Considerable importance should be attached to this where a high standard of excellence is desired.

The nodules of "ironstone" or, more correctly, iron sulphide are a source of considerable anxiety to manufacturers of high-class firebricks. Many attempts have been made to remove these nodules or pebbles by mechanical or other automatic means, but with little success, and the process of hand-sorting still forms the most effective method of removal. Only the coarser impurities in clay, such as stones, nodules, and pieces of roots, etc., may be readily removed by hand, and, as the process is costly, it is worth while to restrict it as far as possible. Thus, much sorting may be avoided in works where several beds of different quality are worked, if these various beds are mined or quarried separately, and care is taken not to mix them. By this means, only the poorer qualities need be sorted, and a considerable amount of trouble and expense may be saved.

The sorting process is usually carried out before the clay is weathered, that is, immediately after it has been dug, so that any injurious materials which are likely to break down and become disseminated through the clay may be removed before the disintegration occurs. A slight weathering of a purely superficial character is in some respects an advantage, as it may result in the formation of a red film of " rust " on the nodules, whereby they may at once be recognised and picked out from the weathered clay. Under such circumstances, weathering is distinctly helpful and desirable.

The removal of nodules and other impurities by picking is generally carried out by elderly men; young men and boys should not be employed on this work, as, being of a more active disposition, they are not so thorough in work of a rather monotonous or irksome character The men should be equipped with hammers of a suitable size, the heads preferably being about 1 lb. in weight. The clay to be sorted is placed in one pile, and the sorter stands on one side, picks up a lump at a time, and throws it on to another pile, or into a wagon, to be taken away to the weathering heap. If a lump feels heavier than one of clay of equal size, the sorter breaks it and removes any nodules which he may find. Where other stones are likely to be present, a rather more careful examination must be made, as they would not be appreciably heavier than clay.

The pickers may be greatly assisted if the clay is delivered on to a gently sloping grid, the bars of which are about 1 inch in width, with 1½ to 2 inch spaces between them. The smaller pieces which cannot be effectively picked pass through the grid, greatly reducing the amount of material to be sorted, and spreading it before the sorters in a convenient manner, which enables them to pick out a number of nodular pieces at once, and thus ensures their removal. Most nodules which are one or more inches in diameter may be removed by hand. It is very important that as much as possible of such materials should be removed before the clay is made up into articles, as otherwise serious damage may result.

It is convenient to sort the clay a second time after a period of weathering, but the cost is usually regarded as prohibitive.

A simple means of removing some of the smaller nodules and relatively hard pieces of material from a fireclay or shale consists in frequently cleaning out the edge-runner mill in which the material is ground. As the harder materials are ground more slowly than the clay and shale, they tend to accumulate on the pan, and if the latter is cleaned out three or more times a day, a very large proportion of the nodules, etc., will be removed in this manner. The material removed from the pan may be screened, if desired, so as to prevent an undue wastage of the clay mixed with the nodules.

Organic matter—largely due to coal-partings and to remains of plants—frequently occurs in fireclays, and, if sufficiently extensive, increases the porosity of the clay, which requires less fuel for burning the bricks, though this is seldom important in fireclays. The hollow spaces formed when the organic matter burns away may cause serious defects in the surface of these goods. Some of the larger pieces of coal or other organic matter may be picked out at the same time as the nodules of iron sulphide, but others, and a variety of other minerals, cannot be so removed. Fortunately, there are many clays which are sufficiently pure to require no treatment beyond careful sorting. The cost of purifying the lower grades of fireclays is generally prohibitive.

The sorted clay is usually stored in the open air, with a rough covering to protect it from rain, if it is to be ground in the dry condition. Where a number of clays are to be used, it is particularly important that they should be dried before weighing out, so that each material may be added in the correct proportion.

Purifying Fireclays.—Many attempts have been made to remove the impurities from fireclay, but no method has yet been devised which is sufficiently cheap to be attractive. Washing is incomplete, and magnetic separators[1] are still less satisfactory, but various processes based on the suspension of the clay in water and allowing the other minerals present to settle have given good results with various clays. The simplest of these processes—which has long been in use in Cornwall in the production of China clay—consists in allowing the water with the clay, etc., in suspension to flow slowly down a long channel at such a rate that most of the impurities will settle out. Plain water is not the best medium for suspending the clay, and by adding a small percentage of water-glass, sodium carbonate, or caustic soda (with barium hydroxide in a few cases), a much better separation is effected. The mixture of clay and solution is allowed to remain stationary for several hours, after which the liquid (with the clay suspended in it) is run off, and the clay in it recovered by one of three methods: (*a*) by evaporating the water on large "floors" heated by fires beneath, (*b*) by adding a coagulant, such as an acid, which will precipitate the suspended clay and cause it to settle rapidly, and (*c*) by the electro-osmose process of Count Schwerin, which is based on the fact that if an electric current is passed through a slip in which the clay is in a colloidal sol state, the clay particles will migrate to the anode, whilst metallic hydroxides migrate to the cathode. Silicic acid and some sulphides are carried to the same pole as the clay—though at a different rate—and are not, therefore, efficiently separated. Most of the mica and felspar are removed by the preliminary process of suspension and sedimentation. In this process, the clay is made into a slurry, a little soda is added, and the whole is subjected to an electric current at 60 to 100 volts. The slip is pumped in a stream through a circular trough, in the centre of which is a revolving drum made of conducting metal, and outside this cylinder, distant about ½ inch or less from it, is a wire-netting cathode, brought right underneath clear of the metal cylinder. Between these the clay is caused to pass. Under the influence of the electric current, the impurities in the clay collect on the wire-netting cathode, whence they are removed either by a current of water, or by means of a continuous worm; the clay collects on the revolving anode and comes off in the form of a thin strip or blanket, 1½ yards wide and about ¼ inch thick. It is stated that the clay thus removed from the cylinder is much more perfectly freed from water than the product from the filter-press, the apparatus generally employed for preparing fine clay bodies.

The nature of the electrically deposited clay depends largely on the speed of circulation of the clay slip; the more slowly it passes the electrodes, the coarser the particles collected on the wire-netting. The density of the deposited material depends on the voltage of the electrodes. Many "good" fireclays are so impure that they only yield about 30 per cent. of fine clay by this treatment, which was patented in 1911 (Eng. Pats. 2379—1911, 3364—1911, 27,930—1911, 27,931—1911; also 159,737—1920).

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[1] The great drawback to the use of magnetic separators is the very fine grinding which is essential if the impurity is to be removed satisfactorily. It is a fact that minute particles of magnetic material can only be attracted and held by a magnet when they are actually in contact with the latter. Hence, the clay to be treated must be ground extremely fine and made into a moderately thin slip. This slip is then passed around and over a number of electromagnets so placed that every particle of the material comes into contact with the magnets. It is not sufficient for the clay slip to flow in a stream over powerful magnets; the slip must be in the form of a thin film, and the magnets must be numerous as well as powerful. The necessity of fine grinding, making into slip, and drying off most of the water in the slip, are all against the extensive use of magnetic separators for the purification of fireclays.

It is important to observe that the electric current plays only a minor part in the purification of clays ; its chief purpose is to effect the rapid deposition of the suspended particles. The actual purification is chiefly (though not entirely) due to the addition of a small proportion of caustic soda, ammonia, or other electrolyte to the slip, in order to retain the clay in suspension whilst the non-plastic materials are allowed to settle. Methods other than electrolysis may then be used to separate the suspended clay particles and the water.[1]

Fireclays which have been purified by any of these methods sinter at a much lower temperature than untreated clays, but have a higher refractoriness, thus giving a long range of vitrification. The melting-point of the purified clay is much sharper, indicating that the separated material is a definite chemical compound. Most clays, when purified by one or other of these methods, differ from crude clays in ceasing to shrink after the sintering is completed, whereas the shrinkage usually continues steadily as the temperature rises. The purified product has also a notably higher plasticity and binding power than the untreated material.

There appear to be great possibilities in purifying some fireclays by first suspending the finer particles in water with the aid of a soda compound, running the liquid from the deposited impurities, and then recovering the clay from the liquid by one of the methods suggested. The great objections are the low yield of clay in many instances, and the great cost of recovering the clay in suspension. A further difficulty is that British fireclays do not usually form a suitable slip unless they have previously been ground to a fine powder, though much more may be done by a blunger of a more powerful type than by those usually employed. The chief drawback to the grinding is the simultaneous reduction of the impurities into a state wherein their separation is made more difficult. The effective admixture of the material with a suitable quantity of water and alkali is not easy on a large scale, and the presence of various impurities in the clay has a marked effect on the properties of the slip. This may be regulated to some extent by selecting a suitable alkali or alkaline earth. The objection that the addition of acid or alkali to a clay slip may increase the fusibility of the clay is not so serious as appears at first sight, as both alkalies and acids are soluble in water, and the proportion held in the pores of the suspended clay is not sufficient to do material harm. It can be kept at a minimum by careful control of the material during the acidification process. It may be necessary to precipitate any sulphates by the addition of barium chloride before adding the sodium carbonate or sodium silicate. There is an optimum proportion of added electrolyte—usually about 5 lb. of sodium carbonate or 10 lb. of sodium silicate per ton of clay. Complete purification of fireclays is impracticable ; the most that can be done is to separate the coarser impurities (see "Casting," p. 611). Wilson and Middleton [2] find that the best separation of quartz and mica is at *p*H 10·5 (with sodium silicate to give free OH′-ions).

J. R. Gront, jun.,[3] has designed an automatic plant.

A modification of the purification of clays by adding an alkali or other electrolyte is used extensively for casting (see Chapter XII.).

An interesting method of purification by *flotation* has been devised by M. C. Shaw,[4] who blunged 5 lb. of clay to a slip of 25 per cent. solids, and

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[1] According to A. V. Bleininger, the purification is really due to the added electrolyte causing the impurities to settle out. The electric current merely affords a means of rapidly depositing the suspended clay. It may be replaced by a mechanical device such as a centrifuge, or by the other methods mentioned above.

[2] *J. Amer. Cer. Soc.*, 1937, **20**, 126.

[3] *Bull. Amer. Cer. Soc.*, 1937, **16**, 387.

[4] *Ibid.*, p. 291.

further blunged with 25 drops each of creosote and paraffin oils. After sedimentation the impurities rose with the oils and the clay settled. Impurities finer than 80-mesh can be removed with 1 pint of oil per ton of clay.

According to M. C. Shaw,[1] the greater part of the impurities in clay can be removed by grinding the clay in a pebble-mill with ½ pint of wood creosote and ½ pint of paraffin oil per ton of clay and with sufficient water to make a slip containing 25 per cent. of solid matter. The mill is emptied and the mixture allowed to stand. The impurities remain suspended in a dark scum on the face of the liquid and can be run off. The creosote and paraffin do not affect the working of the clay or its properties.

Removing Iron and Iron Compounds.—It is always desirable to remove pieces of iron and other obvious impurities before a fireclay is sent to the grinding mills; a long "picking belt" is useful for this purpose, particularly if the upper pulley is fitted so as to act as an electro-magnetic separator. The material must pass over this pulley in a very thin stream, or only large pieces of "tramp iron" will be removed. If small pieces of iron are likely to be present the ground and screened clay should be passed over a second electro-magnetic pulley (see footnote on p. 256).

Many attempts have been made to remove iron compounds from fireclay, but none has been really successful. The addition of an electrolyte (p. 257) is useful, but does not remove the whole of the pyrites, and removes little or none of the soluble iron salts present. It is impracticable to treat the raw clay with hydrochloric acid or chlorine at 900°–1200° C., though this treatment will remove most of the iron from a finely ground clay.

Weathering.—The clay which has been sorted is thrown aside to weather, and water is sometimes applied by rotary sprinklers so as to break down the masses of clay and facilitate the action of the weather. The treatment with water is repeated as often as necessary at suitable intervals. A thorough weathering of the clay is one of the chief and most important factors in the manufacture of really first-class firebricks, and it should seldom be omitted.[2]

The object of weathering a clay is to separate the particles by natural, mechanical, and chemical means, so as to save expense in crushing, and to yield a more convenient product; but in addition to this mechanical advantage many clays undergo marked changes in character on exposure. These changes are usually advantageous, but some fireclays are better if used direct from the pit, as, if weathered, the impurities they contain would be distributed throughout the clay and could not be removed. Some of these clays may be weathered after picking.

Weathered or oxidised iron compounds which have not been washed away by rain soaking into the clay and then being drained off below, are comparatively harmless in the manufacture of firebricks, provided they are not present in sufficient amount to produce undue fluxing effects. Pyrite which has not been decomposed is, on the other hand, a constant source of trouble, as, no matter how finely it is ground, it produces spots of bluish-black slag on the surface and throughout the body of the bricks or other articles containing it, and lowers their market value.

The chief results of exposing clays are a reduction in the density and cohesion of the material as a whole, an increase in its porosity, the oxidation of some of its constituents, and the removal (when water is present) of some of the soluble substances. A number of minor changes, such as the decomposi-

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[1] *Bull. Amer. Cer. Soc.*, 1937, **16**, 293.

[2] Some fireclays (such as the Five Quarter or Bottom Busty seam of West Durham) do not improve on weathering; on the contrary, they become less plastic.

tion of certain minerals by water containing carbonic acid, humic acid, and other substances in solution, and a number of obscure chemical reactions, also occur, together with various physical changes which are largely associated with the colloidal matter present, and are a result of the hydrolysis of the clay molecules. The general effect of these changes is to increase the amount of colloidal gel, to cause it to swell by the absorption of water, and to provide more "lubricant," whereby the particles can slide over each other under pressure. In other words, weathering tends to increase the plasticity of the clay.[1]

Fireclays vary greatly in the extent to which they are affected by exposure; some show a marked difference when exposed in a shed for a single day, but others are scarcely affected by several years' exposure in the open air without any protection whatever. Eighteen months is generally considered the minimum exposure desirable for some shales, and not a few clays must be exposed for years before they are in a fit condition to use.

Many fireclays, in which the iron occurs solely as pyrite, are scarcely benefited by weathering, but if the iron is partly in the form of marcasite or ferrous carbonate (this latter of ill-defined mineralogical composition), the action of the weather on the clay will be to bring about the oxidation of a large proportion of the iron compounds which are less harmful. It is very interesting to note that whilst both marcasite and pyrite have the same chemical composition, corresponding to FeS_2, the former is comparatively easily decomposed on weathering, and is washed out by rain, whilst the latter is scarcely affected. The copper sulphides (chalcopyrite and erubescite) behave like pyrite and marcasite respectively, but form iron and copper sulphates. Selenite and gypsum break up readily under atmospheric influences, and some lime and sulphur are thereby removed from the clay. Alkaline impurities also, unless a high percentage be present, are, to a great extent, broken down and washed away by water, the clay being thus partially freed from these injurious fluxes. Sometimes additional reactions occur as a result of this oxidation, as when pyrite which has been oxidised to sulphate reacts with limestone, forming gypsum and iron carbonate. Sunlight appears to have some effect on clay and to facilitate the oxidation. The difference in behaviour of these various sulphates shows the importance of a knowledge of the mineralogical form, as well as the chemical composition of the impurities occurring in clays before the effect of exposing it to the action of the weather can be predicted.

Stourbridge fireclays usually lie on the weathering beds for two or three years —in some cases seven to ten years—and they should not be used under this period if a reliable article is to be produced, for there is nothing like Nature, viz. rain, frost, snow, etc., for weathering a clay properly. The period can be reduced by passing all the lumps of fireclay through a stone-breaker soon after it has been passed by the sorters and before it is taken to the weathering beds, where artificial means, such as sprinkling with water, can be adopted for getting it into condition. Putting the clay through a stone-breaker is beneficial in other ways, for, although it adds slightly to the cost, this is counterbalanced by the great saving in the wear and tear of the grinding machinery.

So important is weathering in some cases, that bricks made from clay direct from the bank and broken down by powerful machinery will not dry sound, whereas the same clay, after a preliminary crushing and two days' exposure to the air, will make bricks which are in every way satisfactory.

For mechanically breaking up raw clay, no means yet devised by man

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[1] H. A. H. Dunnachie has patented the weathering of Glenboig clay as a means of increasing its plasticity!

have proved so effective as frost, and many works would be closed were it not for the beneficial influence of this agent. Frost acts chiefly by converting the moisture of the clay into ice, which occupies a larger volume than the original water, and, in expanding, it tends to drive the clay particles asunder, whilst the water enveloping these same particles tends to compress them together in other directions by its own expansion. The result is compressive shear and an expansive movement, both taking place at the same time, and producing a result which, if it were only under more complete control, available all through the year, and could be carried out with somewhat less indirect expense, would do much to remove most of the grinding and crushing machinery from the brickyards of this country. Frost is far more powerful in its action than any machinery can be, as with it disintegration takes place from within the particles, rather than from outside them, and produces a number of other effects which cannot be exactly produced by the use of machinery at the present time.

Attempts have been made on a small scale to weather clay by artificial means, but the employment of freezing-chambers has hitherto been found to be far too expensive.

To obtain the best results, the clay should be spread out in thin layers—the thinner the better—so that it may be exposed as fully as possible to the rain and frost, or to the effect of the sun and air which is equally satisfactory with some clays. Some firms tip the clay out of the small wagons or "tubs" in which it has been raised from the pit, so as to form long stacks or "banks," fresh banks being started as existing ones become of too great a length. As each tub is tipped down the bank it is carefully looked over, and all visible bats and lumps of ironstone, often spoken of as "cannocks," are picked out. If possible, the material should be frequently turned over and mixed so as to expose each particle to the action of the weather; and water should be sprinkled on once or twice daily, especially during dry, cold weather, in order that the clay may be capable of benefiting to the utmost when the frost arrives.

Clays vary greatly in the number of times they require to be frozen and thawed to reduce them to a convenient state for working, but it is seldom possible in practice to expose them to more than one intense frost.

It is a mistake to suppose that no weathering takes place except in wet or frosty weather. Many clays simply need exposure to the air for them to break up, and it frequently happens that a couple of days' exposure in dry summer weather will have almost as much effect as subjecting them to a whole winter's rain, frost, and snow. When this is the case, no pains should be spared to secure the advantage so easily gained. Thus it is generally wise to let a fireclay lie in a shed for some weeks before using, as this exposure disintegrates or air-slakes the particles, and distributes the moisture evenly throughout the material. A better and more even colour, and denser goods, can be obtained in this way.

When clay is exposed to air in sheds, the reactions which occur are chiefly of an oxidising nature, as when ferrous compounds are converted into ferric ones by the oxygen in the air. The same reactions also occur when clay is exposed in the open in fine weather. Thus, nodules of "ironstone" which may have been overlooked, or hidden away in large lumps, may, if the clay is exposed to the air, be oxidised on the surface, thus enabling them to be more easily seen and picked out. This is due to the fact that, as the water dries out, it deposits its dissolved salts in patches on the surface of the pieces of clay, and so covers them with a brownish film of limonite and ferrous sulphate. Consequently, a man going over the mound of clay at frequent intervals can readily free the clay from quite a large proportion of its original iron impurity. This cannot occur with purely pyritic compounds, as they are not weathered to anything like the same extent.

A general effect of weathering is to cause the clay to become more open and more homogeneous than when first dug, so that it mixes better with water, and produces a paste which passes more evenly through the machinery. In this way it causes less trouble and increases the output by reducing the number of stoppages and the amount of power needed to work and grind the clay; this saving being, in clays really requiring weathering, greater than the additional cost involved.

After being left to weather during the winter, the clay is often drier, and sometimes has less tendency to shrink in the kiln. More frequently clay which has been weathered has increased in plasticity, and is thereby rendered more valuable.

The reason that wintering the clay has gone out of fashion so much in recent years is chiefly the result of competition, which causes manufacturers to eliminate all processes which do not seem to them to be absolutely necessary.

The expense and interest on capital involved in keeping a large stock of clay is, in a large number of cases, a reason for the clay being made into bricks within a few hours of being mined. The best results must not be expected from such a course, and, where it is possible, several months' supply should be kept exposed. The clay should be spread over as much ground as possible, for if it is in large heaps the inside of these does not get weathered to a sufficient extent. It should be arranged to use the clay as far as possible in regular sequence, so as to give it the benefit of the full period of exposure.

When careful records are kept of the relative cost of grinding and making up clay which has been weathered and of that which has been used directly it has been mined, it is easy to show the saving effected by weathering, even though this exposure of the clay may seem to add so much to the cost. In the first place, a clay which is really worth weathering will be ground at practically double the rate, or with a saving of about one-third of the power required for the fresh clay, so that the saving in fuel in the boiler should alone make up for most, if not all, the cost of weathering, or the increased output with the same quantity of fuel burned below the boiler should produce the same financial result, quite apart from the other advantages gained by exposing the clay. Moreover, in considering the cost of weathering clay it should be remembered that it is always desirable to have a stock of clay on hand in case of accident to mines or trouble with miners.

In place of weathering, or in addition to it, some firms make a practice of grinding the clay, steaming it, and storing it in piles. The purpose of this treatment is not only to soften the coarse grains of plastic clay, and thereby increase its binding power, but also to ensure uniformity in moisture and composition in all parts of the clay.

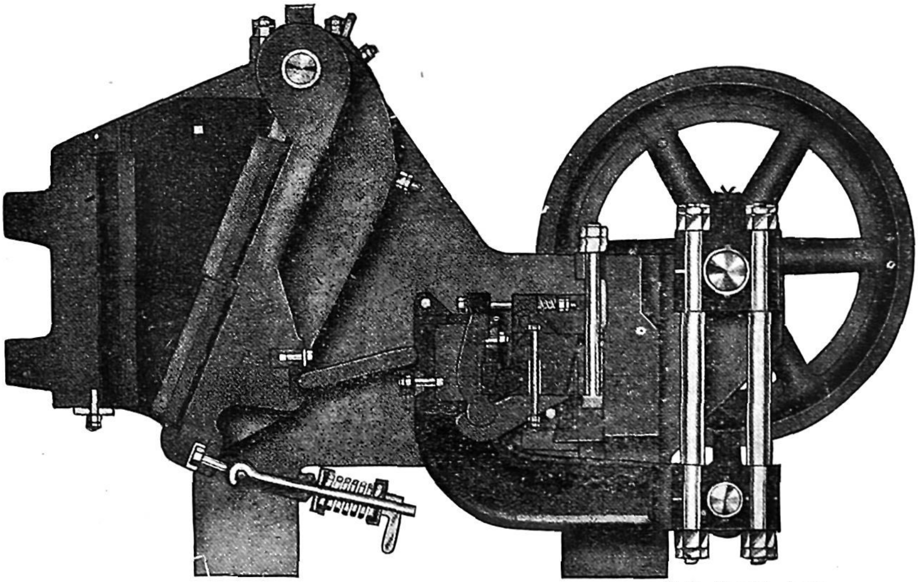
Drying the clay prior to crushing or grinding it has several advantages: it considerably increases the output of the crushing and grinding machinery and affords a much greater control over the size of the bricks. When the clay is crushed, ground, and mixed in its naturally moist state with the addition of such extra water as the youth in charge of the mixer or press may decide, the bricks vary considerably in size and quality. These variations are largely avoided by previously drying the clay. A rotary dryer heated by coke is usually the most suitable.

Crushing consists in breaking the lumps of fireclay into pieces not larger than walnuts, and is a preliminary to finer grinding. Crushing is desirable because fireclays are very destructive to grinding mills—the grids in the revolving pans frequently breaking—so that by adopting a preliminary breaker the grinding plant has a longer life and breakages are minimised.

The crushing is best effected in a jaw-crusher (fig. 36), a rotary crusher (fig. 36A), or crushing rolls (fig. 155), as these machines use very little power in comparison with their output and are much cheaper to use than the edge-runner mills employed for the finer grinding.

The crusher should be placed high enough for it to discharge directly into the feeding device or into the mill.

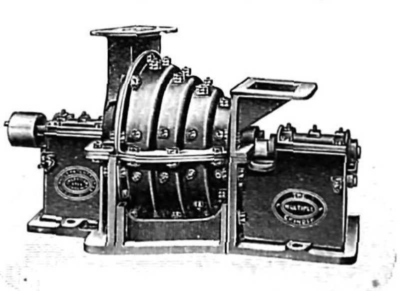
Breaking by hand-hammers has the advantage that impurities which would pass through a crusher may be seen and thrown out. This is important in making goods of the best quality.



H. R. Marsden, Leeds.

FIG. 36.—Marsden's stone-breaker.

Feeding.—The regular feeding of the grinding mill is a matter of great



The Hardy Patent Co. Ltd., Sheffield.

FIG. 36A.—Disintegrator or rotary crusher.

importance, as the output of the mill is very largely dependent on the manner in which the material is supplied to it. The ideal method of supplying clay to an edge-runner mill would be in a continuous stream at a rate precisely equal to the required output, but as this is not usually possible, the feed should be at as frequent intervals as possible. It is obvious that, the smaller the pieces supplied, the greater will be the output of the mill, and in most cases the best and most economical results will be obtained if the mill is supplied only with pieces which will pass completely through a screen with holes 1 inch diameter. It is of great importance that the edge-runners should not be overloaded or the grinding will be hampered, and the machine may be seriously strained by the increased work it is required to do. On the other hand, insufficient delivery seriously diminishes the output.

Where a man is employed to feed the mill by hand, the supply of material is seldom satisfactory, as he either puts too much material into the mill, or he is over-cautious and does not secure the maximum output which the mill is capable of supplying. An automatic feeder overcomes both these defects, as, by its means, a perfectly uniform supply of material to the mill is ensured; but such feeders cannot deal effectively with very large lumps, and should be supplied with material which has previously been passed through a jaw-crusher or disintegrator.

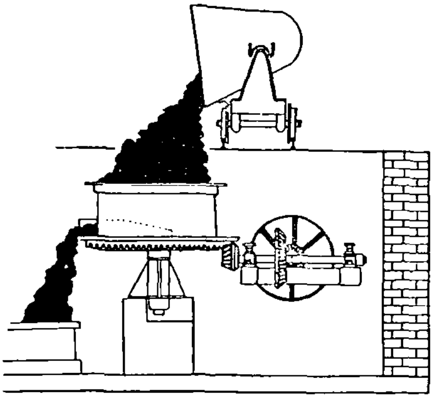


FIG. 37.—Auto-feeder.

Automatic feeders are chiefly of four types—

(i) Screw conveyors, in which the material is tipped on to a horizontal screw or worm and carried forward by it at a rate which depends on the size and speed of rotation of the screw. This type of feeder will deal with plastic clay as well as with shales and fireclays.

(ii) Those consisting of a drum with an independent revolving base-plate (fig. 37), carrying a scraper so arranged that a regular stream of material is delivered through an opening in the side of the drum, or between it and the base, into the mill. The amount of material delivered may be varied by altering the size of the aperture, the speed of the base-plate, or the position of the scraper.

(iii) Those which consist of a conveyor belt above which is mounted a barrier or block, adjusted so as to allow a suitable amount of material to pass beneath it and so fall into the mill. This type of feeder is excellent where the material is fairly uniform in size, and contains few pieces greater than 1 inch and none greater than 2 inches diameter. It is apt to be costly on account of the great abrasion of the belt, but otherwise it is highly satisfactory for fireclays and shales, but not for highly plastic clays. If required, it may be arranged to weigh the clay, as in the Poidometer and Avery feeders.

(iv) An endless belt fitted with buckets or other containers which are automatically filled and discharged at intervals into the mill will not deal satisfactorily with pieces larger than 1 inch diameter, but for smaller pieces it is often quite satisfactory.

The essential characteristics of a good automatic feeder are: (i) strength, (ii) simplicity of design and construction, (iii) resistance to wear and tear, (iv) low driving power, and (v) unlimited capacity to receive and deliver the material in a perfectly regular manner to the mill. Judged by this standard, the two first types of feed are preferable, but rather expensive in power. The drum with a revolving base is excellent in every way for "dry" materials, but it is not suitable for pasty or sticky ones, whilst the band conveyor and bucket elevator are not very durable, and the delivery of the latter is not continuous, but of an intermittent nature, the buckets discharging at intervals into the mill. This is, however, better than hand-feeding, as the amounts supplied are smaller and at more frequent intervals.

The saving in power when edge-runner mills are fed by automatic feeders instead of by hand is very marked. In one case, where the mill was driven electrically and the amount of current was measured, a reduction of 12 h.p. was effected by feeding the clay more regularly and in small quantities at a time. In addition, automatic feeders, when properly regulated, ensure the maximum output from the mill. They also save the cost of a man's wages, besides being more reliable in action.

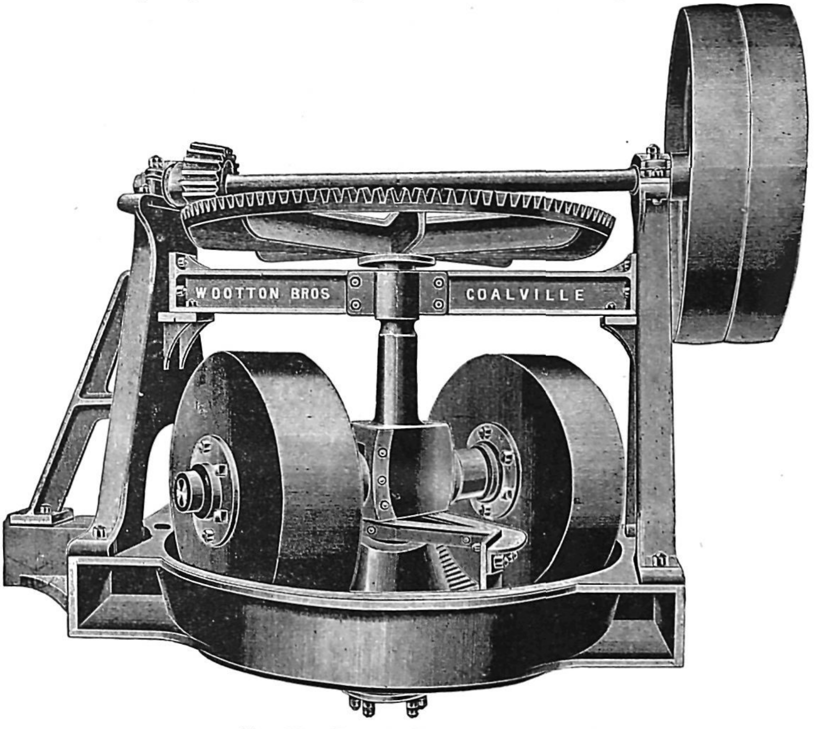


Fig. 38.—Pan grinding mill (chaser mill).

Grinding.—Two kinds of grinding mill are in general use in this country for fireclays; both are of the edge-runner type.[1] The first consists of a pair

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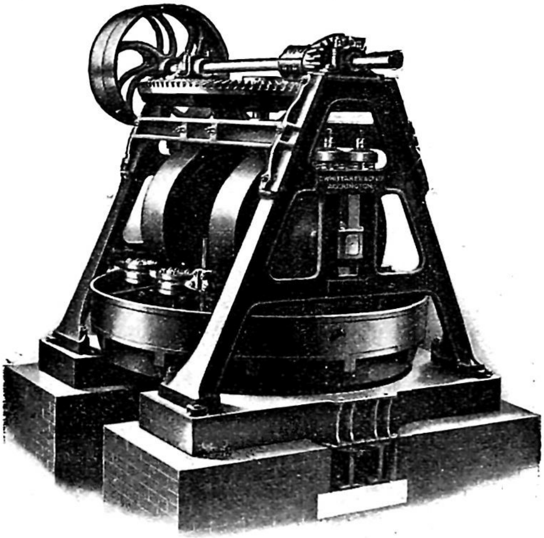
[1] A wet pan is sometimes used, but this is wrong in principle so far as fireclays are con- d, and its use should, therefore, be avoided for *grinding*. The proper method of working o grind the clay, and afterwards to use a wet pan for mixing, if a wet pan is to be used

of edge-runners which roll on a stationary pan fitted with a perforated or slotted bottom, and is sometimes known as a chaser mill (fig. 38). This mill is inferior to the second type for grinding dry clay, but is sometimes superior when grinding pasty clay.

The other mill consists of a pair of edge-runners mounted on a revolving perforated pan (fig. 39), the runners being made to rotate by the friction between them and the clay on the pan. This mill is increasing in popularity, and has so many advantages over other types of mill for grinding fireclays, that its use is now becoming general. It is important that the runners should not be too light, and the whole mill must be well and strongly built. The pan and the rims of the runners should be of steel, and not of iron as is often the case.

The crushing of the clay should not take place on the perforated grids, but on a solid bed formed on the inner portion of the pan nearest the vertical shaft. These pans may be either under- or over-driven, but the latter is the more modern pattern, and is better arranged for inspection, repair, and oiling. The crushed material is spread across the perforated grids by means of properly adjusted scrapers, the smaller grains passing through and falling into a hopper or chamber below. A good pan of this kind will grind sufficient clay to make 20,000 to 30,000 firebricks per day if properly managed, but if badly designed or improperly attended, less than half this output will be obtained. Overloading the mills seriously reduces the output, but it is sometimes practised with clays rich in pyrites, as the proportion of this material which passes through the grids is then lower than when the mill has its nominal load.



C. Whittaker & Co., Ltd., Accrington

Fig. 39.—Grinding mill.

It is a common practice to grind up with the raw clay from one-fourth to one-third of its weight of broken firebricks (grog),[1] so as to reduce the

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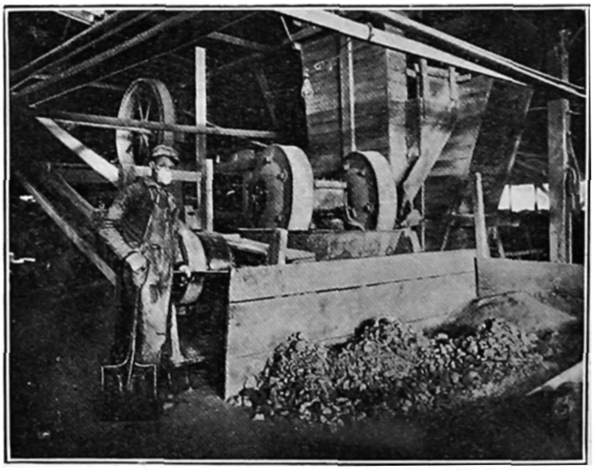
[1] The properties of grog are described on p. 140. Further information on the use of grog in bricks is given later under the heading "Grog Firebricks."

shrinkage of the clay. White sand[1] is sometimes mixed with the clay to reduce its shrinkage. It is much better to grind these materials separately and to add them in a properly ground state to the material just before mixing the latter with water.

In selecting grinding mills, it will usually be found best to have several smaller ones rather than one very large one, as it is then possible to work more in proportion to the output required, and different kinds of material can be ground simultaneously—an important matter when several clays from different sources are used in the production of bricks. The annoyance of having a single large mill, which has to be cleaned out every few days, in order that a different clay or grog may be ground, is very great. It is also possible to work only those mills which are needed during slack times, and the power consumed is notably less when several mills are used in place of one larger one.



(*Courtesy of Mr C. O. Grafton.*)

FIG. 40.—Grinding clay in edge-runner mill.

In selecting these mills, it is desirable to choose them in sizes roughly proportional to the amounts of the different materials used in a typical mixture, so that some economy can be effected by employing a smaller mill for grog grinding than for that used in grinding the most largely used clay. As some grogs are very hard, and are ground but slowly, the difference in size in the mills is not so great as might at first sight be supposed.

The material which has passed through the perforations in the pan is elevated by a bucket conveyor to the screens, where the finer material is removed, and the coarser particles are returned to the mill for further grinding. It is usual to employ revolving screens made of wire gauze with about fourteen holes per linear inch, but the author and numerous firebrick manufacturers, who have tried it, prefer a screen made of sheet steel with $\frac{1}{8}$-inch perforations. This sheet is hung by four chains—one at each corner—at an angle of about

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[1] Sand is bad as a non-plastic material for firebricks, because it reduces the fusing-point of a highly refractory clay, and because it swells on heating, whereas the clay contracts; the particles of sand and clay thus oppose each other and set up internal strains which weaken the goods.

45°, the slope being adjusted to suit the fineness desired. No rapping or other mechanical device is necessary, and this form of screen requires little or no attention.

It is very important that the clay should be properly screened, as any coarse pieces (" nuts ") in it will probably cause cracks or blemishes in the goods. The screens or riddles should be examined frequently, and any necessary repairs should be made promptly. It is also a good plan to pass weighed samples of the screened material through a series of finer screens, and to note the amount of residue left on each. This will ensure that the material is properly graded—a most important factor in the successful manufacture of firebricks.

The sizes of the different particles do not altogether depend on the size of each mesh of the riddles used for sifting the clay as it comes from the grinding mills. Indeed, the riddle merely determines the size of the largest particles, and has no effect in determining the sizes or proportions of the smaller particles, as these are dependent on the nature of the grinding machinery and on the length of time the clay is subject to grinding or crushing.

With the ordinary edge-runner mills, and a riddle with twenty meshes per linear inch, the " tailings " (or clay which passes over instead of going through the riddle) will often, on a further examination, be found to contain a notable proportion of matter which will pass through a sieve of the mesh used, and the sifted material from beneath the riddle will seldom contain more than 7 per cent. of material of a diameter approaching the size of the holes in the riddle. The greater part (often more than 50 per cent. of the sifted clay) will pass through a sieve with sixty meshes per linear inch. Consequently, when a riddle with only six meshes per linear inch is used, the clay will generally be sufficiently fine for resisting frequent changes of temperature during and after firing, though the presence of the coarser pieces sometimes presents some little difficulty to the workman endeavouring to obtain a smooth surface on the work.

If the riddle is incapable of dealing with all the clay put on it by the mill, an excessive proportion of " tailings " is produced, and these being returned to the mill are ground still finer, so that an excessively fine clay is produced. Too short a riddle cannot accommodate the clay, and, by returning too much to the mill, it decreases the output of the latter and produces an excessive amount of " dunted " ware as a result of the presence of too many fine particles in the clay. By replacing the riddle with a longer one of the same mesh, this difficulty would be overcome.

On the Continent, ball mills are largely used in conjunction with air-separators (fig. 42). A flint-lined revolving drum of steel (fig. 41) is charged with flint pebbles and crushed fireclay The pebbles fall on the clay and grind it to powder. The ground material passes out through openings in the mill into an air-separator, in which the finer particles are separated from the coarser ones and the latter are returned to the mill. The air-separator consists of a conical vessel through which a current of air circulates. The material falls on a rapidly revolving plate, from which it is thrown into the air-current. The coarser particles are then separated. By altering the speed of the disc and the air-current, the size of particles separated can be accurately regulated.

It is always preferable to use a wholly externally driven ball mill to one with a central interior shaft. The latter is subjected to a powerful grinding action, and requires frequent renewals.

As air-separators are wasteful in power, the author, under some conditions, strongly advocates the use of a tube mill in conjunction with the ball mill.

The tube mill resembles the ball mill in many respects, but is of such a length that the material passing out of it can be relied upon to be sufficiently fine without there being any necessity to screen it.

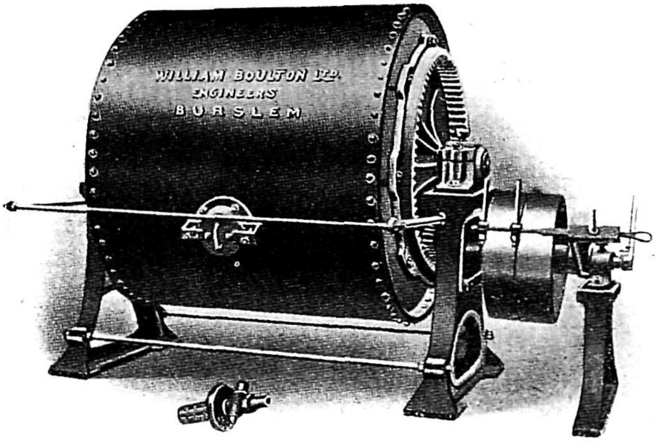

Fig. 41.—Pulverising cylinder.

Highly plastic clays cannot be ground, but must be crushed between parallel rolls placed very close together so as to break up the clay into thin sheets. The addition of grog to these sheets of clay usually enables the material to be mixed or tempered quite readily, though some clays are particularly troublesome in this respect on account of a peculiar stickiness which it is difficult to overcome.

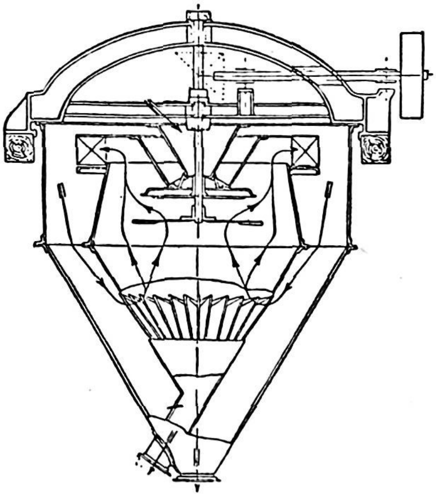

Fig. 42.—Air-separator (Selektor).

The size of the clay particles must be regulated in accordance with the kind of bricks to be produced. Open, porous bricks, of great heat resistance but not intended to carry heavy loads or to withstand the cutting action of flue gases, may be made of coarsely ground clay which has passed through a sieve with ten to fourteen holes per linear inch. For stronger and denser bricks with a more compact surface a finer clay is needed, and this should pass completely through a sieve with twenty or more holes per linear inch.

In grading or sizing the particles to produce a dense brick it is by no means necessary to use a large number of different grades or sizes of grains. On the contrary, the use of five or more grades frequently gives a more porous brick than one made from only two or three grades. The reason is, that when the particles in the various grades are nearly the same size it is almost impossible for them to interlock properly and to fill up the voids sufficiently. Where one coarse and one fine grade is used it is easy to regulate the proportion of each to secure a mixture in which there is a minimum of voids or spaces. For this reason it is seldom wise to use more than three grades of material in the same brick, viz. one coarse, one medium, and one fine grade. The maximum strength is obtained by the use of the largest possible proportion of coarse grog, sufficient medium grog to fill the larger interstices between the larger pieces, and then sufficient plastic clay to coat each particle of grog and provide the necessary bond or "cement." Some fireclays contain so much coarse, non-plastic material that this must be regarded as grog when considering the sizes of the various particles, and it is usually desirable to wash a weighed quantity of ground clay through a series of sieves in order to ascertain the proportion of particles of different sizes. Indeed, the effect of the sizes of the particles of grog and coarse clay employed is so important that careful investigations should be carried out in order to determine exactly what size of grog (if any) is most satisfactory for the particular purpose for which the clay is to be used.

An excellent series of sieves for this purpose consists of seven sieves, each numbered according to the holes per linear inch, viz.: Nos. 6, 12, 25, 40, 60, 100, and 200. When a satisfactory clay or mixture of clays has been obtained, it is passed through these sieves in succession, and the proportion remaining on each is noted. In future mixings the same testing is repeated, and any notable variation is inquired into and the variation stopped. Such variation is usually due to something wrong with the mills or riddles, though occasionally it may be due to the introduction of a different clay.

It is very desirable to test the ground clay and other materials separately as well as when mixed; this gives a more rapid clue to the source of the variation when such variation occurs. The test need only take a few minutes, as about 2 lbs. is ample for a test if a fairly accurate pair of scales is used for weighing the different portions of clay, whilst if 1 kilo. of clay is used and the proportion on the sieves is weighed in grammes, the percentage of each may be found with a minimum of calculation.

Unfortunately, when bricks, etc., are made wholly of a single clay, it is not usually possible to control the relative proportions of different sizes, and all that can be done is to make the test suggested above, and to vary the size of the slots or holes in the grid of the edge-runner mill and the mesh of the riddle, so as to produce a ground clay which corresponds as nearly as possible to the attainable ideal. The usual practice is to use a grid with ⅛-inch holes and a riddle of No. 8 to No. 20 mesh. Much better control and, therefore, much better bricks can be made when grog is used; the manufacture of such bricks is described later in this chapter.

The shape of the particles is almost as important as the sizes, so that the use of materials ground in different types of mills will produce bricks of different densities. Extensive renewals and repairs to an old mill will have a similar effect on the bricks; for this reason it is in every way desirable that the grinding plant should not be allowed to get into a bad state of repair.

No general rules as to the most suitable sizes of grains can be given here, as the conditions under which firebricks are made and used vary so greatly that the materials have to be graded accordingly. Broadly speaking, however, the coarser the grains the better, provided a sufficiently strong brick is obtained and it is not so porous that it is too easily corroded. It is a great mistake to use too fine a material, as this melts more readily than the same material in a coarser state.[1] Some makers produce bricks of an inferior quality from a good fireclay, simply because they grind it too fine and do not use enough grog. They convert the fine clay into a tough, putty-like mass, and thereby make it unduly sensitive to adverse conditions when in use. When a large proportion of grog is to be used, the clay can scarcely be ground too fine; the previous remarks in this paragraph only apply to the use of fireclay with little or no grog.

Steaming.—In the United States it is considered desirable to expose the ground clay to the action of exhaust steam so as to warm and damp it thoroughly without making it really wet. The steamed clay is dumped into bins 12 feet to 15 feet high and stored for a month or more. This practice is not much used in Europe, though the clay paste (see *later*) is sometimes stored before use. Steaming the lumps of fireclay will often enable them to be crushed more easily and to produce a more plastic clay than when the same material is weathered; most manufacturers regard the cost of steaming as prohibitive, though in some cases it is cheaper than weathering as well as more effective (see also *Soaking*).

Steaming is often essential where firebricks are made by compressing semi-dry powder in powerful presses, as the use of water would wet the clay irregularly.

Additional Materials.—Most fireclay bricks are made of fireclay alone but some are made of fireclay and grog and others of fireclay and silica. McKinley and Carter have patented[2] the addition of not more than 5 per cent. of sodium meta-aluminate ($Na_2O.Al_2O_3$), which

(*a*) increases the plasticity;
(*b*) lessens the drying time, drying shrinkage and drying strains;
(*c*) increases the green strength without decreasing the ultimate fusion temperature of the finished article;
(*d*) reduces the porosity of the finished product, or permits the use of a larger grain-size with the same porosity;
(*e*) increases the fired strength of the ware as well as the green strength;
(*f*) increases the resistance to spalling.

The best proportion of each material should be found by careful experiment and should be retained as accurately as possible.

Proportioning.—The usual practice in Great Britain is to add broken bricks to the clay in the mill, the clay and bricks being ground simultaneously. This is a very crude method which is not satisfactory for the highest qualities of firebricks. For these, the clay and grog are ground separately and are screened to the desired sizes. Suitable quantities of each clay and grog are then measured or weighed out and passed to a mixer or tempering mill. Only in this way can the requisite quality be secured. For some purposes, a single clay may prove satisfactory, but more often it is necessary to blend two, three, or more clays with a suitable proportion of grog.[3]

The measuring devices may consist of cars or boxes, or automatic feeders

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[1] In some works, the finest dust is separated by screens and is used for dusting moulds and for "fireclay cement."

[2] U.S.A. Patent 2,019,618 (1936).

[3] C. Robin (Brit. Pat. 17,235 of 1904) advises the use of a composition in which the quantity of alumina is one-fifth to one-seventh of that of the silica, the latter forming 65 to 75 per cent. of the whole material. Thus, if there is 69 per cent. of silica, the alumina should be about 12 per cent.

may be used, according to the output required. Measurement by "shovelfuls" or barrows should be avoided; it is far too inaccurate to be satisfactory. The best plan for a small works is a series of cars or wagons each holding about 3 to 5 cwts., and very deep in proportion to their size. They should be made to hold such a quantity of the clay or other material that there will be no need to use fractions of a car-load in carrying out the measurement of materials for the mixer.

Thus, if the materials are to be mixed in the proportions 20 : 16 : 12, the cars should be made to hold exactly 4 cwts. of each material if the mixing is to be done by weight, but if by volume an exact capacity is not necessary so long as all the cars are the same size.

A car having been filled with the material, a flat wooden bar is drawn over the top (like a strike in hand brickmaking), so as to ensure the wagon being filled to exactly the same extent each time. If this is not done the measurements will not be sufficiently accurate. When less than a car-load of material is required, square boxes may be used and treated in the same manner; indeed, the cars are practically boxes on wheels for their more convenient transport, as boxes need two men to move them, whereas a car, if not too large, needs only one.

It is convenient and economical if the measuring floor is slightly higher than the mixing floor, so that the filled wagons can travel down a slight incline without much labour being required to propel them. It is better still if they will travel automatically.

The measured or weighed materials should be shot on to a floor carefully protected from draughts, and should be mixed together by means of spades. This preliminary mixing is often omitted, but it is highly desirable in the production of the best class of bricks. Instead of hand-mixing, a special mixing machine may be provided, but as two of these are needed—one to be mixing whilst the other is being filled—the hand method is often cheaper in everyday practice.

Various conveyor-mixers are on the market in which a number of worms rotate at different speeds, and so convey the materials forward in the correct proportions to an ordinary paste-mixer or pug. These work admirably, and replace the men needed for the spade work and for the measuring, but they can only be used where one mixture is used for all the goods made, as the alteration of the gearing used to regulate the speed of the different worms is too troublesome and too likely to lead to error to be placed under the control of an ordinary workman.

Whatever method of mixing the dry materials is used, this preliminary work should never be omitted in the production of the best goods, as the ordinary practice of discharging a car-load of a single material, followed by another load of a different material, cannot yield really satisfactory results unless the clay paste is passed several times through the pug mill; and this is needlessly costly, as the friction produced in mixing clays is far greater, and therefore needs far more power, than does the mixing of dry powders. This little point, so often overlooked, is one of the causes of many failures in the manufacture of the best firebricks.

Soaking.—It is usual, after weighing out or measuring the required quantities of each clay or clay and grog, to take them direct to the tempering mill. Sometimes, however, especially where the clay is hard or difficult to saturate with water, it is placed in a pit and soaked in water for 24 hours, or even for several days, in order to distribute the water properly through the mass and to facilitate subsequent treatment. The effect of soaking is much greater if the clay is quite dry than if it is in a moist state, as water penetrates dry clay whilst clay paste is almost impermeable. The soaking pits are usually 10 to 12 feet square and 4 to 6 feet deep, the interior being lined with red bricks cemented together with a cement-mortar and preferably faced with a water-resisting material such as " Pudlo " cement. In some cases, a cement or concrete lining may be quite satisfactory without brickwork, though the latter is usually preferable.

It would be much more convenient in many cases if the pits were built on the surface of the ground instead of being excavated, and were provided with a sliding door or " damper " occupying the greater part of one side, as this would greatly facilitate emptying them. It would increase the cost of construction, but this would be more than counterbalanced by the reduced cost of digging out the clay.

The size of the pit may be increased or reduced if desired, but it is usually better to increase the number of the pits rather than their size, as very deep pits are troublesome in use and more costly to empty, whilst a few pits of very large area do not conduce to such systematic working as a larger number of smaller pits. In estimating the number of pits required, it may be assumed that a capacity of about 4 to 5 cubic yards should be allowed for each thousand bricks per 24 hours soaking, or 1½ cubic yards for each ton of burned ware. Thus, if the clay is to remain in the pit 48 hours, and a daily output equivalent to 8000 bricks is desired, the pit capacity should be sufficient for at least four days, or $4 \times 8 \times 4 = 128$ cubic yards, or $6 \times 8 \times 4 = 192$ cubic yards. It is better to make the capacity of the pits too great rather than too small.

In use, the requisite amount of clay is placed in the pits, and sufficient water is then run in to cover the clay completely. With some clays, an additional amount of water is necessary to allow for that absorbed by the clay. The amount of water required varies with the particular clay under treatment; 40 to 80 gallons per cubic yard of clay is usual. Cold water is generally used, but hot water, or cold water, aided by the injection of steam into the bottom of the soaking pit, is sometimes more effective.

A loose pipe should be provided and connected to the pump or drain, in order that any surplus water may be removed before the soaked clay is taken from the pit.

When two or more different clays, etc., are to be mixed together, they are placed in alternate layers so that they become partly mixed. When the pits are emptied, the contents should be dug from top to bottom so that the various clays, etc., are removed in exactly the right proportions.

Mixing and Tempering.—Most fireclay bricks are made of a pasty material obtained by mixing the clays and grog with water, but the increasing demand for bricks of very accurate shape has resulted in the manufacture of bricks from a slightly damped powder by what is known as the "dry" or "semi-dry" process, described later. In this method, no mixing or tempering is required.

The object of a thorough mixing and tempering is to surround each particle of clay or grog with a film of water, because only in this state is the plasticity of the clay fully developed. Hence, whichever process is used, it should be carried out thoroughly in order to provide a plastic and homogeneous mixture.

The mixing of the materials is one of the most important points to be watched in the manufacture of refractory articles; the best mixing is essential to the production of good work. If the materials are not mixed properly, contraction does not take place uniformly, and strains are set up in different parts of the brick. There is a tendency to less care in the mixing of the material for machine-made bricks than for hand-made ones.

In choosing a mixer for fireclay, everything depends upon the amount of mixing required and the nature of the building in which the work is to be carried on. If the clay is delivered near the ground level, it will probably be best to use a horizontal mixer, and so save excessive lifting of the clay. If, on the other hand, the clay can be delivered at a height of about 6 feet above the ground level, a vertical mixer may be more satisfactory, especially with coarse material, as the natural fall of the material is helpful in reducing the power needed.

The shape of the blades, and their arrangement about the axle, is of far more importance than the vertical or horizontal direction of the mill, and it is preferable to have the clay tried in each of several machines, so as to see which is, in actual practice, the most suitable for a particular purpose.

In a horizontal mixer, the clays and grog are fed in suitable proportions into a horizontal trough containing two shafts, provided with blades (fig. 43) which rotate in opposite directions.

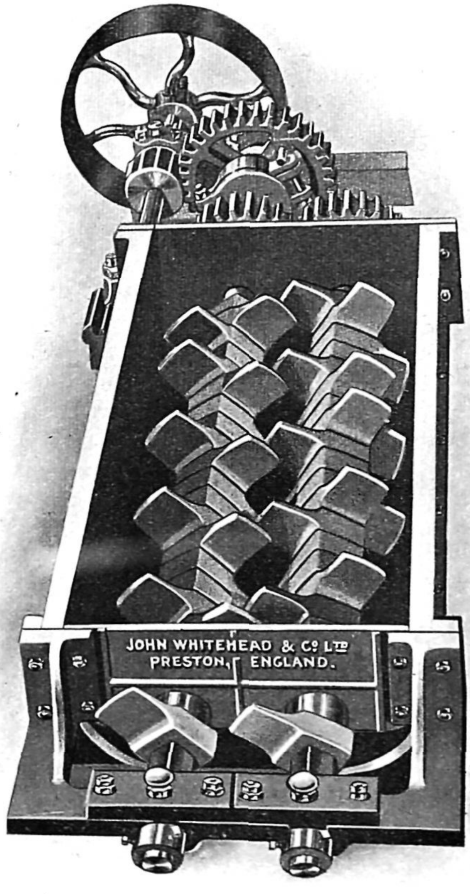
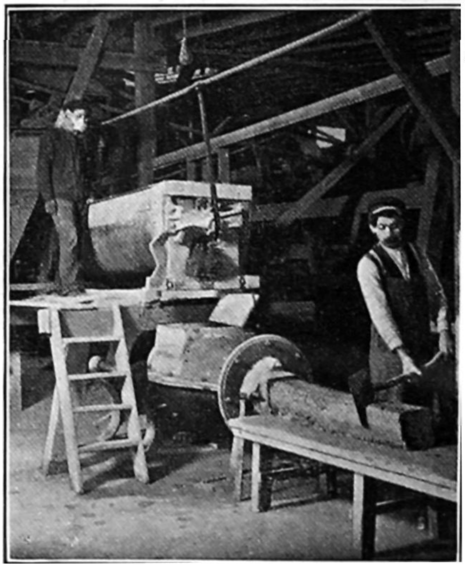


Fig. 43.—Double-shafted trough mixer.

The water is supplied at the entrance end of the mixer in the form of a fine spray, the quantity admitted being regulated by a simple form of screw tap, a shut-off tap being also provided, so as to avoid the disadvantages of using a single tap for regulating and shutting off the water supply. The common plan of a piece of iron pipe closed at one end, and perforated along its length with very small holes, is excellent. The still commoner plan of allowing the water to enter the mixer from a plain pipe outlet (instead of a spray) is not good, and should be discontinued.

With some clays it is desirable to have two, or even three, separate water-sprays at different distances along the mixer, so that all the water is not added at once. This is especially necessary with sticky clays, which absorb an excess of power if they receive too much water at a time. A plan in use in a northern fireclay works, and consisting of a large shallow water tank, into which the clay is tipped and withdrawn by means of elevator buckets in a wet state, does not appeal to the ordinary clayworker as being very satisfactory; but in works in which it is used, it is claimed that the preliminary soaking of the clay enables it to form better bricks than when the water is added in the ordinary way. The amount of water required is a very important factor. Up to a limit which differs with each clay, the greater the proportion of water used in tempering the stronger will be the burned ware, but an excess of water beyond this limit produces weaker ware.



(Courtesy of Mr C. O. Grafton.)

FIG. 44.—Pugging clay.

The addition of a small proportion of caustic soda or sodium carbonate (not exceeding 0·02 per cent.) to the clay just prior to tempering increases the strength of the material by liberating some of the clay in a colloidal form (see *Casting*). Unless the optimum proportion is added, the clay will be difficult to mould.

The mixing is effected by the revolving blades in the mill, which cut up and turn over the pasty material, mixing it thoroughly, and conveying it slowly from one end of the trough to the other. The slower its passage through the trough, the better will the material be mixed; hence, the blades should be arranged almost at right angles to the shaft. A slight angle is, however, necessary, or the material would not progress, but anything approaching the construction of a complete worm or screw-thread arrangement should be avoided, as this carries the clay forward but does not secure adequate mixing.

Instead of an open trough, a closed drum similarly fitted may be used; this is shown as a pug mill (fig. 44). In such a pug mill the length of the barrel should be about four times its internal diameter. As it requires rather less power to drive, an open mixer is generally preferable for the preliminary mixing, but in order to consolidate the clay it should be subsequently passed through either a horizontal (fig. 44) or a vertical pug mill (fig. 45).

Vertical pug mills (fig. 45) are very popular with firebrick manufacturers, though, apart from the fact that they were the first to be invented, and the small ground space they occupy, it is difficult to understand their popularity.

It is often stated that they require less power than an open mixer, but for an equally thorough mixing of the materials this does not appear to be the case. Experiments carried out in 1902 by the author showed that where the mixing is equally thorough, a horizontal mill required rather less power than a vertical one, but that a vertical pug mill will often give a mixture which satisfies the workmen, using less power than a horizontal one. If the product of the vertical mixer is examined carefully, however, it will be found to be rather less uniform, as the material tends to fall through the vertical mill faster than it can be mixed. Mixtures of sharp sand and clay taken from the outlet of a vertical pug mill were found by the author to show much

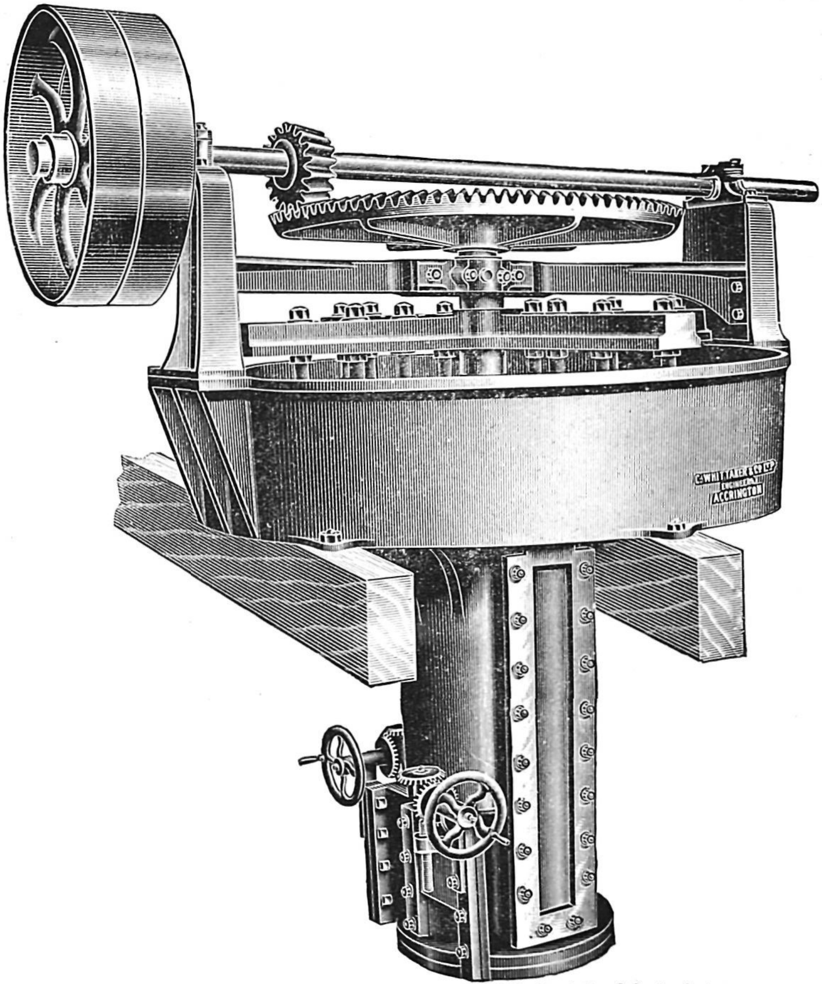


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Fig. 45.—Vertical pug mill.

greater variations in silica (*i.e.* to be less uniformly mixed) than similar materials passed through a horizontal trough mixer, taking the same horse-power and with the same output.

In vertical pug mills, the water should be admitted through a perforated pipe bent in the form of a ring of rather less diameter than the pug mill. A single stream of water should not be permitted, as a series of fine streams gives a better product.

For the soft pastes which are most convenient for hand-moulding, a mixer produces a less uniform mixture than a tempering mill, but it is much cheaper to operate, and, therefore, largely used. Some firms use an open mixer, store the paste for a few days to allow it to " sour," and then temper it in a pan mill. This is an excellent but costly method.

In some works, it is found desirable to put the paste through a second mixer or pug, in order to ensure its complete homogeneity, but this cannot be done with all clays. Some materials would become too plastic if treated in this way, and for these a single mixing must suffice, though a second mixing, whenever it is feasible, is always an advantage; it produces a more complete mixture of the different ingredients of the mass.

For the best bricks, the materials must be mixed thoroughly, as a perfectly uniform mixture is quite essential. Prolonged storage of the paste (*souring*) is equally necessary.

In *tempering*, the measured quantities of clays, grog, and water[1] are placed in a tempering mill. This consists of an edge-runner mill with a non-perforated (solid) revolving pan (fig. 46). The construction of a tempering mill resembles an edge-runner grinding mill, but it is much lighter, and the runners are supported on bearings, so that they *rub* rather than crush the material. Hence, when the mill is empty there is a space of about half an inch between the bottom of the runners and the pan.

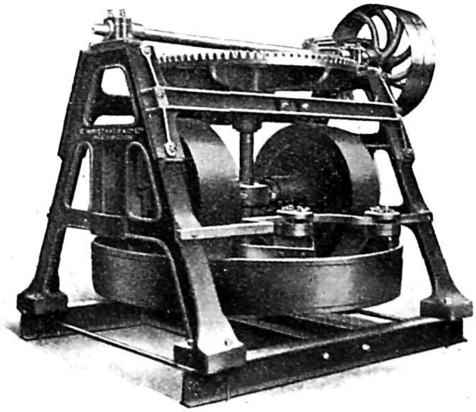

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FIG. 46.—Tempering mill.

The charge or contents of the mill is treated for fifteen to thirty minutes, the pan making about thirty revolutions per minute, and the paste produced is removed by inserting a shovel with a handle about 8 feet long fitting in a swivel joint. This is quicker and cheaper than stopping the mill and taking out the material with an ordinary shovel; but there are risks of the long shovel getting out of control and damaging the workman.

In an ingenious mill in use in a few works, the sides of the pan are fixed and only the bottom revolves. By opening a gate in the side of the pan all the material is discharged from the mill in a simple and efficient manner. A tempering mill manufactured by Thos. C. Fawcett, Ltd., has a fixed pan with an opening beneath, closed by a sliding plate which is operated by a screw.

[1] Some clays work better if *warm* water is used.

To empty this mill, all that is necessary is to open the slide and receive the paste in a wagon placed beneath.

Tempering mills with a continuous delivery are not suitable for fireclays, and should usually be avoided.

In a tempering mill, the materials are rubbed together and a very uniform paste is produced. This rubbing action necessarily results in some of the particles being ground smaller and in their edges being slightly rounded. These are, at first sight, objections to the use of a pan mill, but in practice they occur to so small an extent as to be negligible, and the greater uniformity and higher plasticity of the mixture compared with the product of a pug mill amply compensate for these slight drawbacks.

Another great advantage of a tempering mill is the ease with which different mixtures can be made one after another. A trough mixer requires more time and labour to clean it, and it is less adapted to the mixing of small quantities of material.

The chief disadvantage of a tempering mill is the cost of working it.

Rotary mixers, such as are used in preparing concrete, have been used for tempering fireclay, but without success. They are not sufficiently thorough in their action, and require the material to be more fluid than is convenient to fireclay manufacturers.

Souring.—After grinding, the clay is generally sent direct to the brickmaker, but is sometimes allowed to stand and " sweat " for a few days before use. This maturing (often called " souring ") should take place in a cool cellar, and the clay is then better adapted for the higher branches of manufacture. Further information on this important process is given on p. 115.

Making the Bricks.—The prepared mixture of clays and grog is now ready for making into bricks by one of the following processes : (*a*) by hand-moulding, (*b*) by expression or wire-cutting, (*c*) by the stiff-plastic process, and (*d*) by " semi-dry " pressing. Each of these methods has its advocates, the first being the most popular in Europe, the second being used to only a small extent, the third somewhat more extensively, and the fourth being largely used in the United States.

In **hand-moulding,** a convenient quantity of the clay paste is taken to the moulding sheds, either in barrows or, preferably, in small wagons which run on an overhead track, so arranged that they tip the material on to the bench of the moulder. This man cuts off a lump with a wire bow, rapidly squares it in his hands by " bumping " it several times on his table, lifts it above his head, and then throws it (with a strong downward motion) into the wet or dusted brick mould. This is sometimes of wood, but more often a metal mould, preferably of brass, is used. The moulder then seizes his " strike " (a small straight-edge) and " levels off " the clay in his mould. Sometimes a little grog is sprinkled on the bricks. A " carrier-off " boy takes the filled mould and, turning it, deposits the brick with the flat side on the drying floor. Meanwhile, the brickmaker has filled another mould. The boy returns the empty mould to the man, and, taking the full one, again deposits its contents on the floor. An expert brickmaker usually makes from 2000 to 2500 bricks per day of ten hours, all of which are perfectly solid, and so square that they do not need to be re-pressed.[1] To achieve this result, the clay paste must not be too soft ; indeed, the best moulders use a much stiffer paste for firebricks than for red bricks. To re-press a good hand-made brick is to lessen its value, as the re-pressing sets up internal strains, which become serious

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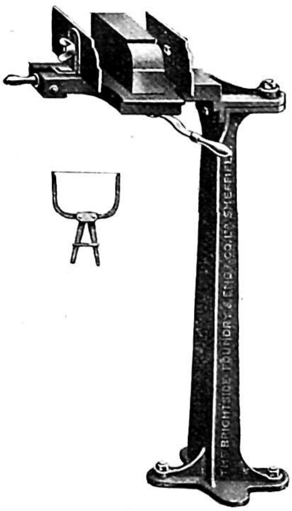
[1] For an illustrated description of various types of re-presses see the author's *Modern Brickmaking* (Benn).

when the brick is in use. There appears to be a similarity between firebrick paste and that used for making tarts and pies, because in both cases great care is needed to keep the paste as light and to work it as little as possible when once it has been produced. On this account, hand working is always likely to be more satisfactory than the use of mechanical means of producing fireclay bricks, as the latter must almost necessarily use more force in the shaping of the bricks than is employed by a skilled workman, and consequently the bricks may be of less value when made by a machine on account of their greater density. At the same time, the scarcity of really first-class makers, and the ever-increasing demands for a lower cost of manufacture, are compelling employers to experiment with various kinds of machines, in the hope that one may be produced which will have a sufficiently light "touch" to produce first-class firebricks.

The facts just given are in themselves ample reason why firebricks for the best purposes should not be pressed after they leave the moulds, but the advantages of cleanness of shape and accuracy of size make it very tempting to makers to give their bricks "just a slight pressure." It is possible to do this with some firebricks,[1] but with many others it is a mistake, as the increase of density is detrimental unless the pressure be so slight as to make it difficult to give the bricks a sufficient sharpness at their edges.

Hand presses, similar to those used for silica bricks, are occasionally used for making clay firebricks, but the rate of production is slower, and the bricks are no better than those moulded by a skilled hand-moulder.

In America, it is customary to use so soft a paste for hand-moulding that the bricks must of necessity be re-pressed after they are about one-quarter dry. Under such conditions, a day's work for a moulder and two boys is 4100 9-inch bricks, the 100 being made to cover waste. The press gang, which consists usually of one man and two boys, follows the moulder when the bricks are black-hard and ready, and the gang presses the same quantity for their day's work. There is another difference between English and American moulding: here, water is used to wet the moulds, and the bricks are slop-moulded; in America, no water is used except to keep the moulds damp, the moulds being dipped in a sand- or grog-trough before each brick is made, so that the bricks are sand- or grog-faced.



The Brightside Foundry & Eng. Co., Ltd., Sheffield.

FIG. 47.—Machine for producing fireclay bricks of special shapes.

A very useful machine for producing fireclay bricks of special shapes is shown in fig. 47. It is very simple in construction, and by means of the two templates of the desired profile, bricks of almost any shape can be produced by drawing a taut wire along the templates. A useful holder for the wire is also shown in fig. 47.

Machine-made Bricks.—Until about 1915 fireclay bricks were almost all made by hand-moulding, the opinion being then held that machine-made

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[1] If accuracy of shape and great resistance to abrasion or corrosion are more important than great refractoriness, it is usually advantageous to use pressed bricks.

bricks spalled and were, in other ways, unsatisfactory. Since that time the manufacture of machine-made firebricks has increased enormously, and few hand-moulded bricks are now made. The machine-made bricks are more accurate in shape, they can be laid with closer joints, and they have a more resistant "skin."

The Wire-cut Process [1] is more extensively used for firebricks in the United States than in this country. A suitable paste is passed into a horizontal pug-mill fitted with a special mouthpiece or die, and the column extruded by this machine is afterwards cut into bricks by means of taut wires. The bricks are soft and must be dried before they enter the kiln. Where accurate shapes are required the bricks are allowed to stiffen slightly and are then pressed mechanically before being dried. An excessive pressure must be avoided; the smallest pressure which will produce the requisite shape is the best.

This process tends to produce laminated bricks unless special precautions are taken. One of the best of these precautions is known as *de-airing*.[2] In it, the paste is consolidated in a horizontal pug-mill, and is then cut into very small and thin slices or shreds and fed into a vacuum chamber from which all the air is exhausted; any air in the clay is thereby removed. The de-aired clay then passes into a second pug-mill, which forms a compact column of clay ready to be cut into bricks. De-airing appears to increase the plasticity and workability of clays to an astonishing extent; the reason for its so doing is not known. The de-aired product is denser and, therefore, more resistant to slag. It is also more resistant to thermal shock. The process is not suitable for mixtures containing much grog or other coarse, non-plastic material as this damages the shredding device, but for ordinary fireclays its advantages are very noticeable.

The shreds or flakes of clay must be so small and thin that they cannot contain any air-bubbles, and it is possible that this shredding is as important as the application of a vacuum.

The employment of soft-mud machines,[1] as might be expected, has proved fairly successful, their action resembling hand-moulding, and the bricks being very loosely made. It remained for the stiff-plastic and semi-dry processes to accomplish what the others had failed to do, viz. produce firebricks of high grades which would stand tests equally as well as hand-made ones and be more accurate in shape.

In the *stiff-plastic process*,[1] the materials are made into a very firm paste, which is moulded under pressure in a clot-mould and is afterwards given an accurate shape in a press. This process is intermediate between hand-moulding and the semi-dry process, and possesses many advantages of both. In it the plasticity of the clay is developed to a much greater extent than in the semi-dry process, so that the stiff-plastic process ensures a strongly bonded brick in which the characteristics of the clay are well developed, whilst shrinkage and liability to warping are reduced to manageable limits and most of the drawbacks connected with hand-moulding are avoided. Consequently, the stiff-plastic process is increasing in popularity among manufacturers, and bids fair to be the chief mechanical method of making firebricks in Europe. The earlier failures with the stiff-plastic process were almost entirely due to

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[1] For details see the author's *Modern Brickmaking* (Benn).

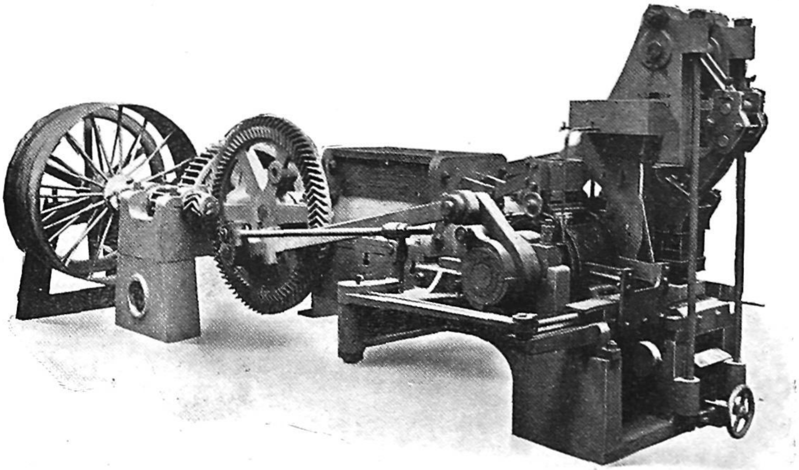
[2] Eng. Pat. 421,531 (1933) seems to be the earliest English patent relating to de-airing *refractory* materials, but the earliest de-airing patent is an American one granted to R. H. Staley in 1902. There is now no patent restriction on the use of de-airing as a process, but the devices used may be patented, and also the application of heat, as in Eng. Pat. 426,662. For a historical sketch of de-airing see E. Lovejoy, *Fundamentals and Economics of the Clay Industries*, Wellesville, N.Y., 1935, p. 343.

using too soft or too plastic a paste, to the employment of mixed instead of "tempered" material, and to excessive pressures; but these difficulties have been now largely overcome.

The machine which is used most extensively for the manufacture of firebricks by the stiff-plastic process is made by Richard Scholefield, and is shown in fig. 48. The methods of using it differ somewhat in various localities, but one which has been found highly satisfactory consists of three stages—

(*a*) Suitable quantities of crushed fireclay,[1] grog, and water are treated in a tempering mill for about fifteen minutes so as to make a somewhat soft paste.

(*b*) This paste is taken to an open trough mixer, and is there mixed with about half as much clay[2] as was used to make the paste.



R. Scholefield, Leeds.

FIG. 48.—Stiff-plastic brick machine.

(*c*) The stiff-plastic mixture is passed through the small pug mill of the machine shown in fig. 48, and thence into moulds in a rotating cylinder, these moulds being filled and discharged automatically and the clots passed into the press in front of the machine, where they receive their final shape and are taken away to be dried. The bricks so produced are plastic, and yet so stiff that considerable pressure must be used to make a thumb-mark on them. They possess all the advantages of bricks made of plastic clay, with the exception of a slightly greater density, and are much more accurate in shape than hand-moulded bricks. Attempts to avoid the use of a tempering mill and those in which the whole of the clay is tempered have yielded unsatisfactory results;

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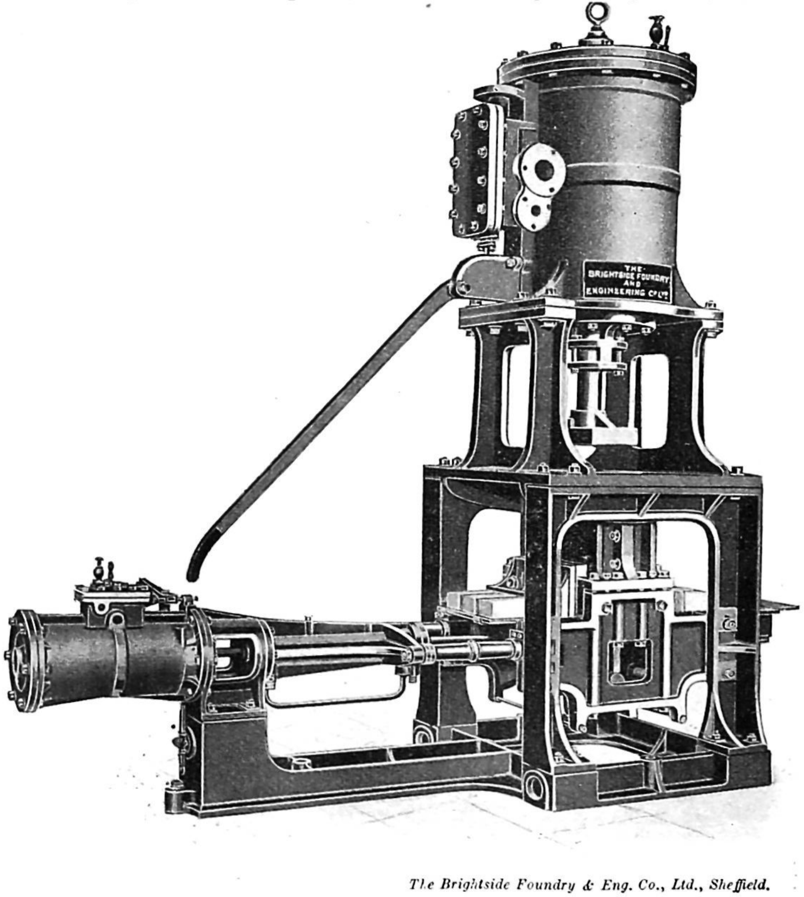
[1] This clay should have been passed through a $\frac{1}{4}$-inch mesh riddle so as to keep it sufficiently coarse. The fine dust should be separated by passing the clay over a $\frac{1}{24}$-inch riddle, and is used later. If a sufficiently long $\frac{1}{4}$-inch mesh riddle is used, a second screening may be unnecessary, as the fine clay will fall through the first third of the riddle and so will automatically separate itself from the coarser clay.

If too much fine clay is present, the bricks will be too dense and unduly sensitive to sudden changes in temperature.

[2] It is convenient to add the finer particles of clay at this stage.

the former do not produce sufficient uniformity and plasticity in the bricks, and the latter produce a material which is too soft to be pressed properly by the machine.

A press intended to produce bricks similar to hand-made ones is shown in fig. 49, and made by The Brightside Foundry & Engineering Co., Ltd. The clay paste is placed in a deep box, and is then compressed by a single piston so as to fill three moulds at a time. The reciprocating table which carries the moulds is then moved, and the bricks are delivered automatically on to a pallet, and a second set of moulds is brought into position beneath the clay-box. The machine is then ready to make three more bricks. When the container is almost empty, the piston must be raised and the container refilled with prepared clay. This machine may be worked either by steam (as shown) or by hydraulic pressure.



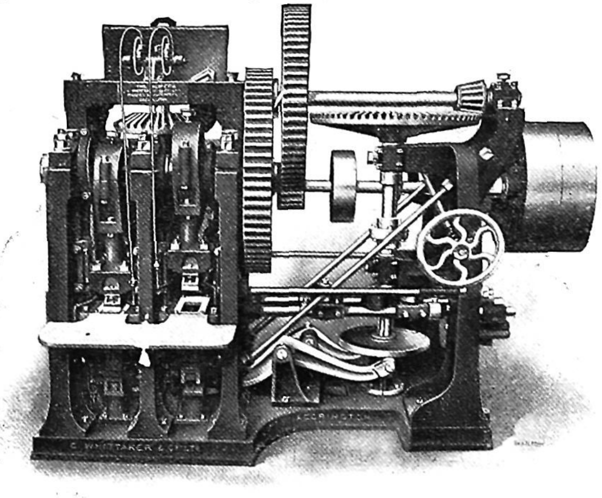
The Brightside Foundry & Eng. Co., Ltd., Sheffield.

FIG. 49.—Steam-operated press.

Other machines have also been used successfully for making firebricks by the stiff-plastic process. In the one made by C. Whittaker & Co., Ltd.

(fig. 50), the prepared material is fed into a hopper and is discharged into a vertical pug mill, which mixes the clay and drives it into one of two clot-moulds, each being alternately brought under the pug mill exit, the other being, at the same time, under the plunger of the press. There are two presses, and the bricks are fed into each alternately, only one press being in operation at once. The advantage of this method is that the action of the press is continuous, the mould boxes being moved backwards and forwards. The makers state that no more power is required to work the two presses than would be required for one, whilst the time required for pressing is considerably less. The moulds and sliding parts are lubricated by means of an oil-spray worked by a pressure blower.

Sliding-die machines have an advantage over drum machines, because the clots have a flat instead of a slightly curved face, and sliding-die machines require less power than those having rotary tables.



C. Whittaker & Co., Ltd., Accrington.

Fig. 50.—" New Era " brick press.

In Germany, large numbers of firebricks are made in presses with rotating tables containing four moulds. The presser lays a previously made clot in one of the moulds, the table then makes one quarter of a revolution and the clot is pressed automatically; the table then makes a second quarter-revolution, and the brick is automatically lifted out of the mould and removed by hand. The mould is oiled at its next quarter-turn and is then ready to be refilled. This machine resembles the machines used in this country for making stiff-plastic bricks, but differs from them (i) in the use of a hand-made or wire-cut clot instead of filling the mould direct from a vertical pug mill; (ii) in the absence of a re-press independent of the rotary table. An English machine which closely resembles the German ones is the Hercules press, manufactured by Herbert Alexander & Co.

The oil used for lubricating the moulds or dies of brick machines is usually a mixture of paraffin with a little thick engine oil or colza. Another good and cheap oil is made by mixing 5 lbs. of melted lard of the cheapest variety obtainable with each gallon of paraffin.

Instead of oiling the press-box, it is sometimes more convenient to place the clot on a pad of felt supplied with oil prior to placing it in the press. The oiled surface of consecutive clots should be placed alternately uppermost and lowermost in the press.

Some machines employed for stiff-plastic building bricks have not proved satisfactory for fireclay bricks, owing to the manner in which the moulds are filled and the excessive and repeated pressure applied. By omitting the re-press and supplying the press operating directly on to the rotary table with clots formed by hand or in a wire-cut machine, these objections may be overcome. It would be still better if some firm making "stiff-plastic" brick machines with rotary tables would design a special machine of this type for fireclay bricks, avoiding the defects (due to excessive pressure, etc.) caused when existing machines (which are highly satisfactory for building bricks) are used for firebricks.

Although the stiff-plastic process may seem cumbersome, it is extremely simple if properly managed, but it requires skilled supervision when it is first started.

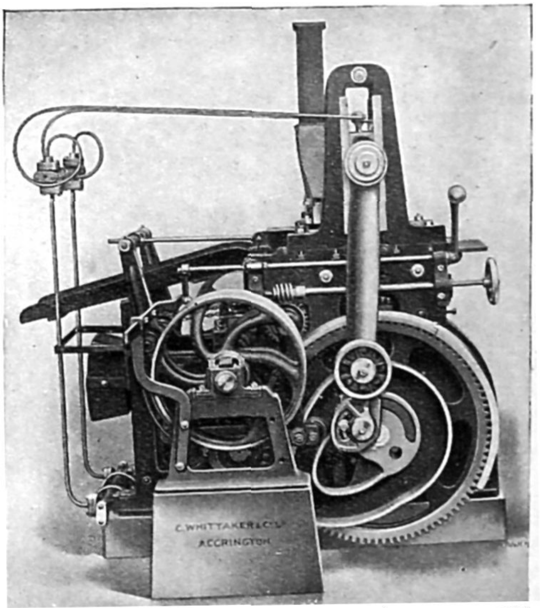
In the *semi-dry* process, the material supplied to the press is in the form of a slightly damp powder which only requires to be pressed to give it the desired shape.

The *advantages* of the semi-dry process for firebricks are the high initial strength combined with accuracy of form, which enables a minimum of jointing material to be employed—a circumstance of importance in the stability of firebrick masonry, as thick fireclay jointing contracts in the firing, and tends to shatter the structure. In addition to this, the granular texture of the bricks has a beneficial influence on their expansion and contraction when heated. Bricks made by this process will give much better results on crushing, but they require to be burned at a much higher temperature than hand-made firebricks, as the bond is so much feebler. The higher temperature of burning is accompanied by other advantages, such as lesser shrinkage in use, so that *properly made* semi-dry process firebricks are amongst the best firebricks produced. The reasons that so many attempts to make firebricks by this process have been unsatisfactory are: (*a*) improper treatment of the raw material, (*b*) insufficient pressure, (*c*) incomplete burning, (*d*) careless or improper handling previous to burning, and (*e*) use of the bricks for unsuitable purposes. For instance, dry-pressed bricks are not adapted to resist abrasion or slag action.

Other *disadvantages* of this process are: (*f*) somewhat greater cost of equipment; (*g*) greater cost of repairs to machinery; (*h*) higher fuel consumption in the kiln; (*i*) the bricks have a low resistance to abrasion, are very absorbent and less durable where they come in contact with water or with molten slags, dust, and flue-gases.

Semi-dry clay has a strong grinding action on the *moulds* or *dies*, and these must be kept in good order or the bricks will have bad edges. With badly worn dies there would be no pressure around the edges and at the corners, and without pressure there would be no primary bond, and the edges and corners would crumble off in handling, either before or after burning. In one of the best machines (made by C. Whittaker & Co., Ltd., Accrington, fig. 51), using this process when applied to building bricks, the ground and screened material from the mill and mixers is fed into the hopper of this machine, and thence by means of a sliding box into the first mould. The amount of material received in the mould can be regulated instantly, so that as the dampness of the material varies from time to time, more or less clay can be taken into the mould. The brick, after having two pressures put on to it, is automatically fed into the second mould, and there it is pressed again; thus it is subjected to four distinct pressures, each pressure being about 80 tons. This machine has an output of 5000 to 6000 bricks per day, and, according to the makers, requires 5 horse-power to drive it. It should be noted that in this machine no oil is used to lubricate the moulds. Unfortunately, this machine exerts far too great a pressure to enable it to be used to the best advantage for most *fire*-bricks, though by carefully adjusting the pressure, it has been used satisfactorily in a few firebrick works.

The Stanley patent semi-dry or dust machine is made by the Nuneaton Engineering Co., Ltd., and is shown in fig. 52. This machine is altogether different from the type mentioned above. The dust is fed from a reciprocating charger in the usual way, but the pressure is applied by means of shaped cams working on rollers fitted with cross-heads, carrying on their lower sides plungers which fit into dies. Pressure is gradually applied, and during the process is slightly relieved, allowing the escape of air and the equal expansion of the clay dust in the die. At the finish of the pressing stage the top plungers and dies are forced down on to the stationary bottom plungers, regulated to a greater or lesser height as required. This simple action gives the bottom, sides, and arrises as true and hard a finish as the upper parts of the brick. As the feed-boxes fill the die they deliver the pressed bricks to the front, giving ample time for the attendant to remove them.



C. Whittaker & Co., Ltd., Accrington.

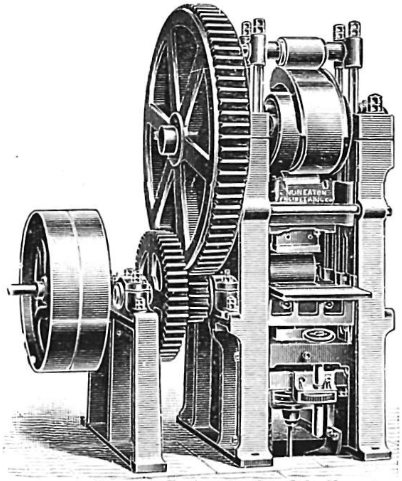
FIG. 51.—Press for semi-dry process.

In its latest form, the machine is fitted with two die-boxes and plungers, so as to make two bricks at once, and with lifting-fingers which lift the brick and carry it forward to the delivery table, where it is placed down gently, and the fingers travel back to receive a second brick. This arrangement preserves the arrises from the damage which is inevitable when the bricks are pushed along to the delivery table.

The machine is also fitted with a special charging appliance, which takes the form of a false bottom in the feed-box which supplies the clay to the die. In the ordinary form of feed there is an unavoidable tendency to produce bricks with one soft end, owing to the manner in which the clay is fed into the die. In the new arrangement the false bottom is closed until the box is completely over the die, when it opens from the centre outwards, fills the die with the dust, closes and carries the box out of the way of the descending plunger.

A press of an entirely different type is the "Emperor," made by Sutcliffe, Speakman & Co., Ltd. (fig. 53). Though primarily designed for materials devoid of plasticity, this press is well suited for some fireclays worked in a dry or semi-dry state.

It consists of a horizontal, rotating table, containing the moulds arranged singly or in pairs, and, depending on the size, there are from six to eight pairs of moulds. The table is rotated in such a manner that whilst one pair is receiving the charge of material to be pressed, another is under pressure, and a third is over the discharge ram. The feeding is quite automatic, being effected by means of a circular pan in which revolves a series of stirrers which prevent the material choking, and ensures a regular and constant feed. The quantity of material fed into the moulds is regulated by means of a hand wheel, and, as this can be turned whilst the machine is in motion, the pressure can be regulated at will. The pressing mechanism is of the toggle-and-knee type, and the distribution of the pressure is so effected that massive steel bolts take all the greater strains of the framework. Ample adjustments are made for taking up wear and tear. The moulds are on the "economic" principle, and are easily relined, as in putting in new liners no fitting or adjustment is required. Each set of liners can be reversed, giving two wearing faces.



Nuneaton Engineering Co., Ltd., Nuneaton.

FIG. 52.—Stanley press for semi-dry bricks.

This press can be made to give a top and bottom equal and simultaneous pressure, or to give a bottom pressure only, or a quadruple pressure, the final pressure being greater than the first.

A patent expression attachment (fig. 53A) operates by giving each brick two pressings: the first squeezes and presses the material from the centre into the corners and arrises: the final pressure finishes the brick. By these means each brick is of even density throughout, with fine, sharp corners and arrises. Fig. 53A shows one brick in the mould receiving the first or preliminary pressure, and another the final pressure.

When used for brickmaking, the goods are delivered on the table for removal by the attendant, and are not pushed forward as in some presses of the vertical type, but an automatic pusher-off can be attached to the machine to deliver the bricks on to a travelling band if required.

This machine has a maximum output of from 1000 (single type) to 2400 (duplex type) bricks per hour. The power required to operate it is from 5 to 12 horse-power. It works smoothly and easily, and, owing to powerful springs, shown clearly in fig. 53, it is evenly balanced. These springs are not for relieving the pressure, but merely to balance the heavy pressing mechanism, and, if desired, the machine can be run without them.

It is very difficult to produce a sound firebrick by the semi-dry method without applying too much pressure, but M. Curry and W. O. Wood in 1915 patented the use of a pad of indiarubber on which the loose bottom of the die is allowed to rest, and claimed that by this addition the objections to pressed firebricks are overcome.

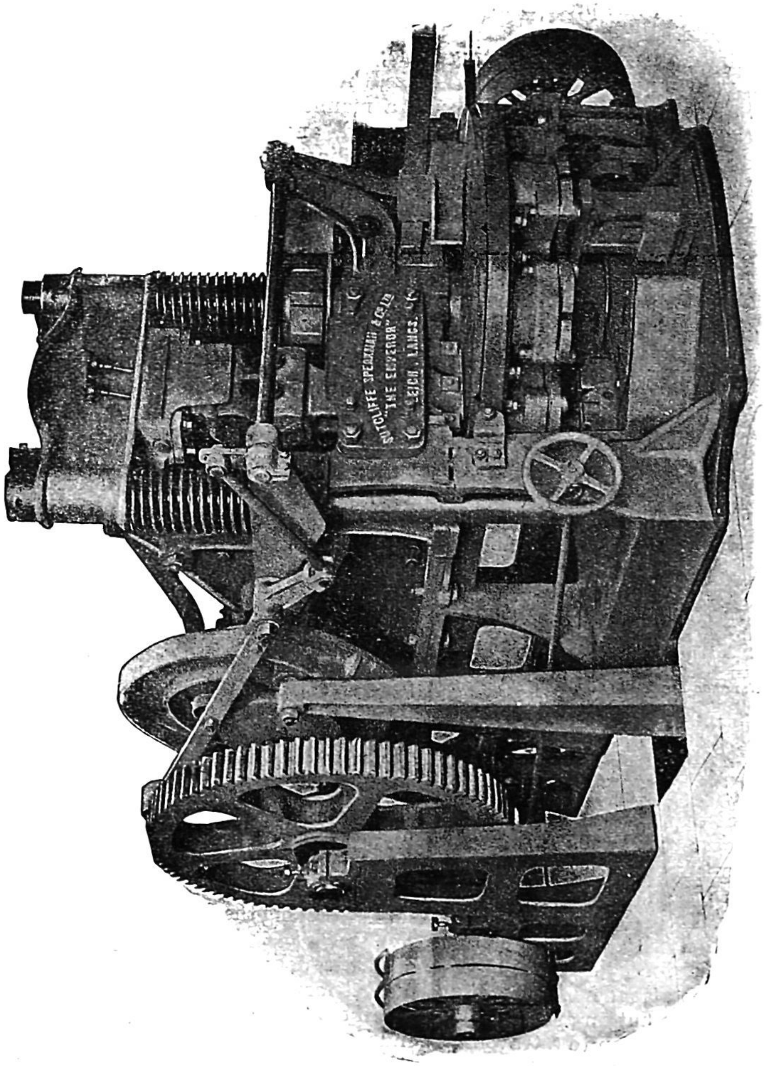
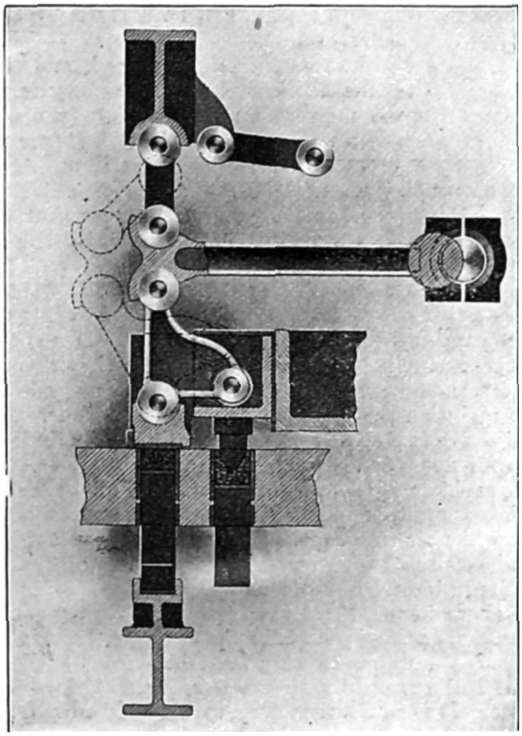


FIG. 53.—"Emperor" press.

Sutcliffe, Speakman & Co., Ltd., Leigh, Lancs.

The difficulties in working the semi-dry process are often exaggerated. By far the most important is *lamination*, which is recognised by the production of thin layers of material, easily visible when a brick is broken, which cause the brick to split off or spall in certain directions. It is not often due to insufficient pressure, but may be caused by excessive pressure if this is applied at the wrong time. In many instances, the cause of lamination is very obscure, but insufficient treatment of the material is a prominent factor, especially if the clay is obtained dry and is damped and imperfectly mixed later. This produces portions of material in which the plasticity is strongly developed, whilst in others it is scarcely developed at all, and lamination consequently results. One brickmaker of the author's acquaintance has compared it to the use of flour in preparing puff-pastry. "The dough is rolled out into thin pieces, and sprinkled with flour, and then rolled again. On placing it in the oven, the dry flour causes the plastic layers of dough to part from each other, and the laminated character of puff-pastry is thereby obtained."



Sutcliffe, Speakman & Co., Ltd., Leigh, Lancs.

FIG. 53A.—Action of "Emperor" press.

The manner in which the pressure is applied is very important, for, as pointed out by Lovejoy, it is essential to remember that on any machine in which the plungers approach each other and squeeze the clay towards the centre of the mould, the brick will show a comparative granulation on this centre plane, due to a lack of density, quite noticeable even at some distance. "If the pressure is all from the top, the granulation will be at the bottom, and its position will depend upon the relative degree of motion of the two plungers." This granulation is often attributed to included air, and all machine manufacturers provide for its escape, either through air-holes in the plunger plates or by releasing the pressure before the final pressure is applied.

The stiff-plastic and semi-dry processes of firebrick manufacture have come to stay. Some men will make a failure of either, through lack of proper knowledge or equipment, but each has advantages which must be recognised by any impartial investigator. Neither should be adopted exclusively, but there are many firms now employing the hand-moulding process who could profit by the use of machinery.

The following conditions are essential in both the stiff-plastic and semi-dry processes when used for firebricks :—

(i) The clays and grog must be thoroughly mixed, and the sizes of the particles so graded that the finished brick has a suitable texture.

(ii) The moisture in the mixture must be uniformly distributed. This is best effected by the use of a water-spray in the stiff-plastic process and by steaming in the semi-dry process, as liquid water is difficult to distribute evenly through a semi-dry mass. The proportion of water present should not usually exceed 15 per cent. as compared with 20 per cent. in the material used for hand-moulding. As a soft paste can be made homogeneous more easily than a stiff one, it is more convenient to shape the clots of soft paste either by hand-moulding or in a wire-cut machine, and then to allow them to dry slightly so as to reduce the proportion of water to that which will give a material which can be pressed satisfactorily.

(iii) The pressure applied to the bricks when in the press must be ample, but on no account should it be greater than is really needed for shaping. It is important to maintain the pressure for a sufficient time. A rapid blow is not nearly so effective as a steady pressure continued for three seconds, and a steady pressure for five seconds produces still better bricks. Fireclay bricks produced by too rapid an application of pressure are brittle, and liable to spall. Usually it is necessary to apply two or more pressures, with an interval between to allow the air to escape. It is still better to apply the pressures in different die-boxes so as to ensure a perfect release of the air. Failure to secure this results in imperfectly pressed bricks, which are too weak to be of value, as any air surrounding the particles prevents their union.

(iv) If the bricks, as they come from the press, are too friable, either more clay must be used, a more plastic clay must be substituted, or the plasticity of the clay must be increased by more water, steaming, or prolonged storing in a moist state. It is not satisfactory to use only raw clay for firebricks made by the semi-dry process.

(v) Some dry-pressed bricks on the market are defective through being underfired.

In comparing these various processes it should be observed that each one will make bricks better suited to some kinds of work than others, and that all the methods may be used with advantage in different branches of the trade. The selection of a process suitable for a given clay or a particular class of firebrick is, therefore, a matter for expert advice which is independent of the makers of the machines.

The risk of machine-pressed bricks spalling and falling to pieces more readily than hand-made ones only occurs in connection with the most severe conditions under which such bricks are used, so that for the majority of the purposes for which they are employed, the pressed bricks are quite as serviceable as hand-made ones, and in some instances they are even superior. This is particularly the case where the chief property desired is a high resistance to corrosion, and, consequently, bricks with a close surface and thin regular joints will prove more durable than those with a more open texture and wide and irregular joints. When resistance to sudden changes in temperature is the chief consideration, hand-made bricks are usually superior to machine-made ones.

Re-pressing.—The reasons for re-pressing bricks are twofold: (*a*) to improve their shape and (*b*) to increase their density. Both reasons are, to some extent, a confession of failure, because if the bricks are machine-made re-pressing should not be needed, and if the bricks are hand-made re-pressing is particularly undesirable (see p. 277).

Presses for re-pressing are usually provided with " escapements " through which the surplus clay escapes. These are convenient, but are liable to cause cracks. It is, therefore, better not to re-press bricks which are much oversize and to avoid the use of an escapement. The surplus material can be used in varying the size of the frog in the brick.

Drying.[1]—After the bricks have been made they must be dried by artificial heat. The only exception is that of bricks made by the semi-dry process, such bricks being removed from the press, placed on trucks mounted on good springs, and taken direct to the kiln.[2]

Firebricks made from a plastic paste may be dried on hot floors or in heated chambers or on trucks which are passed through heated tunnels.

As most firebricks will stand fairly rapid drying, but are very sensitive to small shocks, it is usual to dry them on steam- or fire-heated floors, or in rack dryers, and not in tunnels. Automatic wagons for placing the pallet boards and bricks on the drying racks and removing them therefrom are extensively used on the Continent, but are scarcely ever seen in this country; this is unfortunate, as they are very satisfactory.

Tunnel dryers are used on the Continent with satisfactory results in many cases. The use of cars on which the bricks are dried is unquestionably cheaper than racks or hot floors, but the cost of installation is heavy.

Dryers in which heat from the kilns is used are commonly considered to be the most economical, and some firms dry the bricks on top of coke ovens and similar structures, where a large amount of waste heat is produced.

The drying floor most generally used consists of a series of flues about 15 inches wide and 9 inches deep running the whole length of the floor, and covered with iron plates or with concrete slabs about 1 yard square. The joints between the plates or slabs should be made steam-tight, with a very lean mortar made of cement and sand. The walls forming the flues are usually of bricks, placed slightly apart so as to form checker-work. Exhaust steam (or live steam at a pressure not exceeding 10 lbs. per square inch) or the heat from coke fires or kilns enters a cross-flue at one end of the dryer, travels through the flues to a cross-flue at the other end, and finally escapes up a small chimney shaft. By means of steam taps or dampers various parts of the floor can be allowed to heat or cool, and the temperature can be regulated to suit the needs of the bricks or other goods being dried. Iron plates enable the bricks to be dried much more rapidly than do concrete slabs, but some clays will not stand so rapid a heating. On the other hand, a concrete floor will remain flat for a much longer time, and the bricks dried on it will be less liable to damage by irregularities in the floor. Whichever material

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[1] Further information on the principles of drying and the construction of dryers will be found in the author's *Modern Brickmaking* (Scott, Greenwood & Son) and *The Clayworkers' Handbook* (Griffin).

[2] Bricks made by the stiff-plastic process are sometimes (though unwisely) taken direct to the kiln.

is used, the floor should be kept in good condition, or the bricks will be badly shaped. It is essential that the drying shed should be well ventilated without being draughty, as otherwise drying will be very slow.

The design of a drying floor should be regulated by the nature of the clays and the speed at which they may be dried. It is, therefore, necessary to make a careful study of the individual materials, and it is seldom wise to erect a large dryer or drying floor without obtaining expert advice on the subject. A drying floor which is admirably suited for fireclays in the Newcastle district is less satisfactory in Scotland, and *vice versa*, and neither pattern would be suitable for highly plastic clays without making some modification in it.

It is often convenient to have the dryer on the "first floor" instead of on the ground ; this dryer is supplied by a vertical endless elevator provided with projecting arms which carry the pallet boards on which the bricks are laid as soon as formed.

In firebrick-making on a very large scale, where many thousands are made in a day, some expeditious method of drying is essential, and it is desirable to have the bricks dry and in the kiln within at most forty-eight hours from the time of making.[1] Although any suggestion for a longer time than this to be occupied would almost certainly fail to gain more than a moment's consideration from a manufacturer, yet it is not sufficiently known that the refractory quality of clay wares is sensibly improved by slow drying and long seasoning in the dry-house, and that bricks dried slowly on a steam-heated floor are consequently of better quality than those dried more rapidly in a tunnel. Provided the output is large enough, and that the bricks are not damaged by the shocks to which they are generally subjected in a tunnel dryer, this form will be found to be the most economical, especially if it is heated by exhaust steam and by waste heat from the kilns. With very sensitive clays it may be better to dry the bricks on pallets placed on racks in a modified tunnel or chamber dryer, the most suitable design depending, as already mentioned, on local circumstances and on the characteristics of the clay to be dried. The most rapid drying consistent with safety is effected in what is known as a *humidity dryer*. In this chamber the bricks or other articles are stacked on cars or shelves, and are first heated with air which is saturated with moisture until they attain a suitable[2] temperature below that of boiling water. So long as the air circulating through the dryer is saturated with moisture no drying can occur ; all that happens is that the goods are heated to the required temperature. After this, part of the saturated air is replaced by fresh air at the same temperature, and this replacement is continued progressively until the goods are fully dry. They are then cooled by circulating air of diminishing temperature. Various modifications of this procedure are used so as to avoid unnecessary costs, but the essential principle should be retained. The most delicate bricks can be dried with certainty by this means in 48 hours, and many bricks can be dried more rapidly. Fireclay bricks which are " easy " to dry do not need a humidity dryer of an elaborate type, but a simple form is usually far more economical than the customary hot-floor or tunnel dryer.

Too rapid drying is very injurious to fireclay bricks and blocks.

For objects of moderate size the rate of drying is approximately proportional to the ratio of surface to volume. Objects of large size, however,

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[1] In some works, four days are required to dry firebricks on a steam-heated floor. This is usually due to defective ventilation of the drying shed.

[2] There is an optimum temperature for each article.

take much longer to dry, and require the application of a considerable amount of heat to complete the removal of all the water of manufacture from the interior. Many large goods made of fireclay require extremely careful treatment, and have to be kept in a heated atmosphere for several weeks after the moisture has apparently all been removed. Disastrous results are frequently known to occur in the steaming operations in the kiln for want of sufficient care in this particular. Manufacturers frequently adopt a wise precaution in having such goods stamped with the date of making, and in holding their workmen responsible if they are rendered unsound by being burned before the lapse of a stated period of drying.

The use of a humidity dryer enables large articles to be dried safely in a much shorter time; in some cases several weeks are saved when such a dryer has been properly adjusted to the requirements of the articles.

Large blocks should be allowed to *mature* before commencing the drying.

Formulæ have been suggested for finding the *safe rate of drying*.[1]

In order that the goods may not twist or warp when drying, it is essential that they should shrink very little. This means that very little plastic clay can be used in the material, although some is necessary to bind the particles together and to give it the general characteristics of clay. With a carefully compounded mixture the contraction from paste to entering the kiln should not exceed 1 inch in 16 (or ¾ inch per foot). If it does so, more non-plastic material must be added. The lower the shrinkage, the better the chance of the bricks coming true out of the drying rooms; hence, as much non-shrinking material as possible should be used in clay mixtures so as to keep the shrinkage at a minimum.

Tensile tests on a dried clay, alone or mixed with various materials, are often made in order to gain an insight into the best means of enabling a clay to resist the strains produced in drying. They show that the clays capable of resisting the largest strains are those which contain particles of various sizes rather than consisting of wholly fine or wholly coarse ones.

Like all active colloids, plastic clays part with water extremely slowly, and by decreasing the general porosity of the material, the plastic portions retard the evaporation of water not actually entangled in them. The presence of large quantities of non-colloidal materials, such as grog, increases the rate at which clays may be safely dried, and, where suitable, materials of this kind are usually added. If the clay is in large pieces and is at all dense, it will crack unless special precautions are taken in the application of the heat used in drying.

The removal of the moisture is accompanied by a reduction in the volume of the clay mass (see *Shrinkage*) and a temporary loss of plasticity. Both of these can, however, be restored on adding water to the clay, provided that the temperature to which the material has been heated is not sufficient to convert any colloids present into irreversible gels or otherwise to destroy the structure of the clay.

When a clay which has been mixed with water is left in a dry atmosphere the water evaporates progressively. As long as the body preserves a sufficient plasticity the departure of the water results in the grains of clay coming closer together in proportion to the volume of water removed, but when there is no longer sufficient water to allow the grains of clay to become displaced, the shrinkage ceases, and the evaporation of the last portions of water causes the formation of pores in the interior of the mass.

The dry body thus obtained no longer resembles the original clay; it

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[1] H. H. Macey, *Trans. Brit. Cer. Soc.*, 1939, **38**, 464–475.

forms a harder mass of a greater density, and the molecular attraction continues to be so powerful after the departure of water that, unlike other (non-plastic) mineral powders, it retains its form and does not fall into powder when dried.

The bricks must remain in the dryer until all the water added in the preparation of the clay has been driven off and the bricks are hard enough to set in the kiln. It is very important that the bricks should be well dried, or they will not be satisfactory.

Although, by sending bricks made by the semi-dry process direct to the kiln, the drying process with all its troubles is apparently eliminated, it is found in practice that " semi-dry " bricks need as careful drying as any others, the only difference being that it is carried out in the kiln instead of in separate dryers. The reason is that in " plastic " bricks the plasticity of the clay is well developed and the granular particles are cemented together, but in the semi-dry clay the bond is largely mechanical. The colloid properties are not developed, and, if the particles are connected at all, it must be with dust, and at best imperfectly. When the pressure is applied the particles are forced together and into each other, and held there by interlocking, assisted, of course, by whatever colloid properties may have been developed. The dust fills the interstices under various degrees of pressure, according to its amount, the protection it has received in the interlocking of the particles, and the opportunity afforded for the escape of the air during the final pressure. The air in escaping may also sweep clean the points of contact of the inter-locking particles and still further reduce the strength of the goods.

Bricks held together by such a delicate bond must be very carefully dried in the kiln from three to twelve days, and in some cases (as with large blocks) two or three weeks are required. It is more a sweating process than a drying one, so slowly is the moisture taken off. Rapid drying would loosen the particles, which would not reunite in burning, and the result would be a rotten brick.

Flatting.—When hand-moulded fireclay bricks have become partially but not completely dry, and are in what is known as a " black hard " or " leather hard " condition, they may be flatted, rapped, or pressed slightly on a small rotating table in order to overcome any tendency to warp in drying. It is often sufficient, with larger pieces, to turn them over so that any tendency to warp may be prevented by this inversion, but smaller pieces should usually be pressed or beaten lightly.

In a few special cases, it is found that the slight pressure produced by a weight on a board placed on top of an article is invaluable in preserving the desired shape and in preventing portions from rising above the main body on account of internal tension.

Coating.—It is not at all usual in this country to supply firebricks which have one side or end composed of, or covered with, a different material, but on the Continent this is becoming more and more common, as there is a considerable demand there for bricks which will resist specific influences. To make the whole of the brick of alumina, magnesia, or other material would prove too costly in many cases, so fireclay bricks are supplied with the necessary portions " protected " by a coating of reasonable thickness.

Carborundum coatings have also been used very satisfactorily for increasing the refractoriness of firebricks (see Chapter VIII.). M. Barrett and the Leeds Fireclay Co., Ltd. (Eng. Pat. 103,953 of 1916), suggest that the surfaces of refractory bricks may be made more resistant by salt glazing them at a temperature above 1300° C., and any parts which are not required to be glazed may be previously coated with a wash of barium sulphate.

The use of glaze on firebricks to resist the action of acids, etc., comes legitimately under this head, but as such bricks are not usually regarded as firebricks they need not be further considered here, it being more or less accidental that they are made of fireclay.

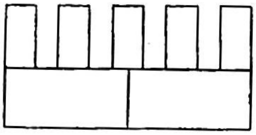

FIG. 54.—Setting.

The coating may be applied by pressing a thin slab of the material into the end or side of the mould before making the brick, or by making the coating material into a slip with about an equal weight of water and either dipping the bricks into this or applying the slip to the bricks by means of a brush or spatula.

Transport.—The barrows or cars employed for wheeling the dried bricks to the kiln should be well designed and provided with good springs so as not to damage the bricks during transit over rough ground. Many firebricks are spoiled by the numerous small shocks they receive as a result of the use of unsuitable barrows or cars.

Setting is the term used for placing the bricks in the kiln in such a manner that they will be heated satisfactorily. This depends to some extent on the kind of kiln used and on the shape and sizes of the bricks or blocks. They should be arranged with a space between each, in order that the hot gases may circulate uniformly around them, and to secure the evaporation and gasification of all volatile matter in the bricks.

A very suitable method for all the kilns ordinarily employed for burning firebricks is to set the bricks on the narrower sides with about ⅝ inch between each. The correct spacing is found by placing five bricks as headers across two stretchers,[1] as in fig. 54, and to keep as many bricks as possible, one above the other, in this direction. To secure stability it is necessary to place a row of stretchers right across the kiln at intervals as shown in fig. 55. There should only be sufficient rows of stretchers to "tie" the bricks effectively; additional stretchers only hinder the efficient heating of the kiln. When a kiln is filled with bricks they will appear as shown in fig. 55. It is sometimes necessary to set the bricks a little closer in certain parts of the kiln so as to overcome the otherwise unavoidable differences in the draught of the kiln, and to leave rather larger spaces near the bottom of a Newcastle kiln or a continuous kiln (see fig. 55); but, speaking broadly, the more uniformly the bricks are set the better they will be burned. Different workmen employ

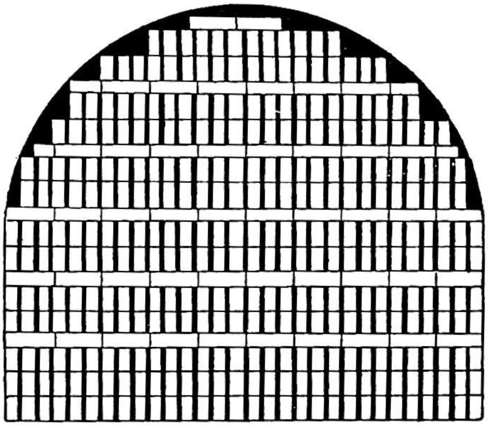

FIG. 55.—View of Newcastle or continuous kiln, when set.

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[1] This only applies to bricks 3 inches thick; narrower bricks should be set ⅜ inch apart.

slight variations from the foregoing, but the one just described constitutes the best *general* arrangement; it may, of course, be modified to suit special needs.

A matter of great importance in setting firebricks is to avoid overcrowding the kiln. In down-draught kilns the greater part of the dome or crown should be left empty to allow the proper combustion and distribution of the fire gases. This cannot occur if the kiln is filled completely to the crown, and irregular heating, accompanied by waste of fuel, is an inevitable result of such overcrowding. In a Newcastle or continuous kiln, on the contrary, a space about 3 feet wide must be left between the fire and the bricks, but in these kilns the bricks may be set close to the crown. The reason is that in down-draught kilns the hot gases and air first combine at the top of the kiln, whereas in horizontal-draught kilns the combustion occurs closer to the fires.

Kilns.[1]—The kilns used for burning firebricks are of many forms, but these may be arranged in three main groups according to the chief direction in which the fire-gases travel, viz. (1) up-draught kilns, (2) down-draught kilns, and (3) horizontal-draught kilns.

In *up-draught kilns* the fires are arranged near the base, and the gases from these enter the bottom of the kiln and rise upwards until they finally pass out through the opening in the roof. It is difficult to obtain a sufficiently high and uniform temperature for the proper burning of firebricks in kilns of this type, so that down-draught and horizontal-draught kilns are generally preferred. The latter are also more economical in fuel.

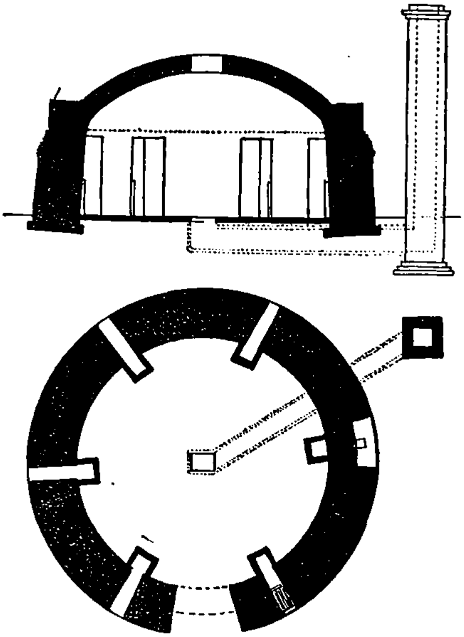

FIG. 56.—Round down-draught kiln.

Down-draught kilns (fig. 56) consist of a brick chamber which may be either circular or rectangular in plan, covered with an arched roof or dome commonly termed a "crown." A convenient size holds 16,000 bricks; much larger kilns are used for building bricks, but are not economical at the far higher temperatures required in burning firebricks.

The fires are placed uniformly on the circumference of the round kilns or along each of the two longer sides of rectangular kilns. The gases from these fires pass through the walls of the kiln and rise upwards through a series of small open-top chambers termed "bags," from which they issue with some velocity and strike the crown of the kiln. From thence they are deflected downwards, passing among the bricks, eventually entering a series of flues beneath

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[1] Only the more important kilns are mentioned in the following pages. Readers requiring information about other kilns should see the author's *Kilns and Kiln Building* (Clay-worker Press, Essex Street, London, W.C., 1916).

the floor of the kiln and connected to the main flue leading to the chimney.

Opinions among the makers of the best firebricks differ greatly as to the most suitable form of exit for the flue-gases, and in different parts of the country differences in practice are very great. This is curious, as kiln construction is only to a minor degree related to the nature of the clay to be fired when the temperature to be reached and the time of heating are at all comparable.

In down-draught kilns the uppermost bricks are heated first, but the distribution of the heat is very uniform, and with care no part of the contents need be heated excessively. By controlling the admission of air to the crown of the kiln the temperature can be regulated with great accuracy.

Both round and rectangular down-draught kilns are used extensively for burning firebricks, particularly in Yorkshire, the Midlands, Scotland, and Wales.

It is essential that the flues be of ample size, and the draught—whether produced by a chimney or a fan—be more than is really needed, it being much easier to partially close a damper, if the draught prove excessive, than it is to burn firebricks satisfactorily in a kiln which is short of draught. Owing to the greater ease of regulating the draught under adverse conditions of wind and weather, a fan is often preferable to a chimney.

The most suitable form of grate is stated to be a combined flat and sloping one, the air-supply being regulated by the amount of fuel on the sloping portion. The number of fire-boxes will, naturally, depend on the size of the kiln ; there may be as many as twenty or as few as four, but the usual number is eight.

It is a great advantage if the floor of the kiln is on the same level as the trucks in the railway siding, and if the distance from the latter is as small as possible. If temporary rails are laid from the trucks to the kiln the loading is further facilitated.

For many reasons, it is better to perforate the whole of the sole of the kiln, and to remove the gases from parts scattered throughout the whole surface; but this kind of sole is often regarded as unsatisfactory because of its comparative weakness to wear and tear, and most manufacturers are content to have four groups of holes in the floor through which the gases may pass out of the kiln.

Instead of using a separate chimney, as shown in fig. 56, some manufacturers prefer a cone or cupola erected on top of the kiln. When this is used the gases pass through a series of radial flues beneath the floor and then rise through vertical flues in the kiln wall into the cupola above. This type of kiln is particularly favoured in Lanarkshire, where it is regarded as giving a more uniform heat than the type shown in fig. 56.

The chief disadvantage of single kilns is the amount of fuel they require in proportion to the weight of the goods burned. More than 60 per cent. of the heat from this fuel passes up the chimney, but can be recovered by connecting the kilns together so as to pass the waste gases from one kiln into another, and repeating this until the temperature of the gases is too low to make their further utilisation desirable. It is difficult to connect round kilns in a satisfactory manner, but rectangular ones can be built side by side in groups so that the connecting flues are exceedingly short. Where the output is only sufficiently large to require six kilns, the saving in fuel which can be effected by connecting them together will be about 40 per cent. of the total fuel burned in the single kilns. With a larger number of chambers a saving of 60 per cent. of the fuel can be assured without in any way interfering with the quality of the goods or with the customary manner of burning them.

One frequent cause of failure in connection with the firing of refractory clays in kilns which have been connected so as to make them continuous or semi-continuous in action is the faulty design of the connecting flues. These are, in most cases, made too small in cross-section and too long, and they usually take the gases from the wrong parts of one kiln and discharge them into an incorrect part of another to be heated by them. For some mysterious reason most people, when altering kilns or in attempting to connect up chambers with one another so as to form a kind of continuous kiln, imagine that the entering gases should be admitted from the top of the kiln. This is quite erroneous, and is certain to lead to failure, as it is opposed to several well-known properties of hot gases. The best rule to follow in such cases is to admit the hot gases as nearly as possible at the same place as they would be produced if an ordinary solid fuel were used. Thus, if the ordinary grates or fire-boxes of the separate kilns are at one or both ends, the hot gases should be admitted by flues opening into the kilns at one or both ends, and as near to the fire-boxes as possible.

Instead of connecting the kilns to each other, the waste gases may be used to heat a drying floor.

A good example of a *continuous kiln* on the down-draught principle is the Ruabon kiln, patented by W. Jones & Sons, part of which is shown in section in fig. 57. As will be seen, it consists simply of a series of rectangular down-draught kilns, in which the fire-gases are passed through one chamber after another instead of going directly up the chimney and being wasted.

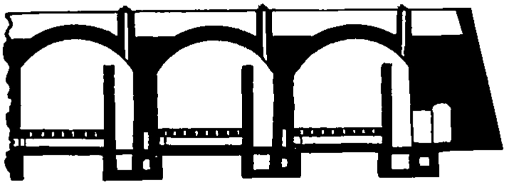

Fig. 57.—Jones' Ruabon kiln.

Gas-fired down-draught kilns are particularly satisfactory for burning firebricks and other refractory goods. The fireplaces are replaced by a series of gas burners, and air heated regeneratively is supplied for the proper combustion of the gas. The gas is made automatically in a producer, and the chief advantages of its use lie in its cleanliness, greater uniformity of heating, efficient, and therefore economical, use of the fuel, and reduced wear and tear of the kiln. If the kiln is properly designed and well constructed there are no drawbacks to the use of gas for burning refractory bricks, but, unfortunately, many patents have been obtained for useless designs of gas-fired kilns, and not a few of these kilns have been built so badly as to prove useless. Ignorance and poor workmanship are chiefly responsible for the slow progress which gas-firing has made in burning firebricks. This is in marked contrast to the steel industry, where gas-firing is extensively used for the furnaces built of the very bricks for which the manufacturers consider it is necessary to employ coal!

A typical gas-fired down-draught kiln for firebricks is shown in fig. 58. This was designed by E. Schmatolla, and found to be specially suitable at temperatures higher than can be obtained by direct firing with coal.

It consists chiefly in the connection of the heating chamber with two or more heat-collectors, accumulators, or regenerators; the furnace proper is arranged so that it may be started as a direct fired grate, and afterwards changed gradually to gas-firing, and on this account it is built centrally to the whole structure, the regenerators being placed at each side.

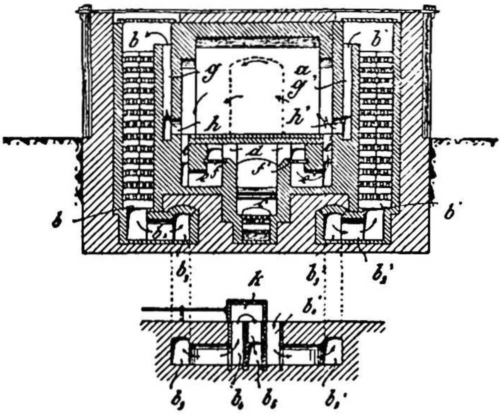

FIG. 58.—Intermittent gas-fired kiln.

The gas generator (c), which is built in a similar manner to a grate, but with a higher shaft, is arranged below the burning chamber (*a*), and the two heat-collectors or accumulators reach approximately from the bottom end of the gas generator to the upper end of the heating or burning chamber. The gas generator is connected to the chamber at both sides by means of conduits or flues (*d*, *e*), between which are arranged dampers (*f*), the latter making it possible to close either of the two gas-flues (*d*, *e*). The two heat-collectors (*b*) are connected to the heating or burning chamber (*a*) by means of conduits (*g*) and openings (*h*). The heat-collectors, which are provided with a filling of refractory bricks or other material, are connected at the bottom end to conduits (b_1, b_2, b_3, b_4), which can be brought into communication either with the chimney channel (b_5) or with the outer air by means of a device consisting of a box (*k*). Assuming that the damper (*f*) on the left-hand side is closed, the corresponding damper on the right-hand side being open, and the box standing as shown in the drawings, the conduit (b_4) on the right-hand side is in connection with the outer air, and the conduit (b_4) on the left-hand side is connected with the chimney; and assuming further that the generator is filled with coal, and that the whole furnace is already incandescent, the generator gas will then pass through the right-hand conduit system (*d*, *e*) into the heating chamber (*a*), and the air through the right-hand conduit system (b_4, b_3, b_2, b_1), the filling of the right-hand collector, and the conduits (*g*, *h*), also into the heating chamber (*a*). Gas and air become mixed at the right-hand end of the chamber, burn in the interior of the chamber (*a*), and pass at the other end through the conduits (*h*, *g*) and heat-collectors (*b*), as well as the conduits (b_1, b_2, b_3, b_4) on the left hand, into the chimney. The combustion gases escaping from the chamber give off the greatest portion of their heat to the brickwork of the heat-collector arranged on the left-hand side. When the latter is so highly heated that the combustion gases begin to escape through the flues (b_1, b_2, b_3, b_4) at a higher temperature, the box (*k*) is drawn to the right side, so that the left channel (b_4) is open, and the right channels (b_1, b_2, b_3, b_4) are connected to the chimney. If, then, the right-hand damper (*f*) is closed and the left-hand one is opened, the gas will pass through the left-hand side flues (*e*) and (*g*) into the chamber, and the air will pass through the left-hand side flues (b_4, b_3, b_2, b_1), the filling of the left-hand side heat-collector, and the right-hand side flues (*g*, *h*), into the chamber. The direction of the flame will be reversed, and it will pass on the other side through the flues (*g*, *h*) to the heat-collector, and after having given off to the latter the greatest portion of its heat, through the right-hand flues (b_1, b_2, b_3, b_4) into the chimney. The air is, of course, highly heated by the previously highly heated left-side accumulator, and passes into the chamber at a very high temperature. The producer gas will also pass into the heating chamber at a very high temperature, since it has to traverse only a short conduit, and thus it is possible to increase the temperature in the chamber to a much higher degree than is possible in the furnaces generally used and almost to the limit of the dissociation temperature of carbon dioxide—that is to say, up to 2000° C.

Various modifications of this arrangement, in which the air is heated by passing it through tubes inserted in the main flue so as to form recuperators, are also in use and have proved fairly satisfactory. The temperature attained by the air in this case is not, however, so great as when the ordinary regenerator is used, as brickwork is an abnormally bad radiator and conductor of heat.

It is important to notice that whilst heat regeneration is of the greatest value when kilns or furnaces are fired by gas, a considerable saving may be effected by supplying the kilns with hot air even when coal is used direct.

The principle of a regenerator is comparatively simple. It consists in passing the hot flue-gases through a mass of brickwork arranged in the form of a series of grids or tiny flues (fig. 59); these flues become heated by the passage of the gases through them, so that when the gases are shut off and a current of air is substituted this air becomes very strongly heated. In practice, it is necessary to have two regenerators and to use them alternately—passing air through one and gases through the other, and changing every half-hour or so.

Fig. 60 represents a down-draught kiln with such a regenerator, the flue-gases passing down through the perforated sole in the direction shown by the arrows, through the narrow slit-like flues to the main flues (f), and so to the chimney. At the same time the air used for the combustion of the fuel is drawn in at the ground level through underground flues (f_1, f_1), and then through the alternate flues of the regenerator (a, a, b), and in the combustion chamber (l, l) meets with the gases from the fuel.

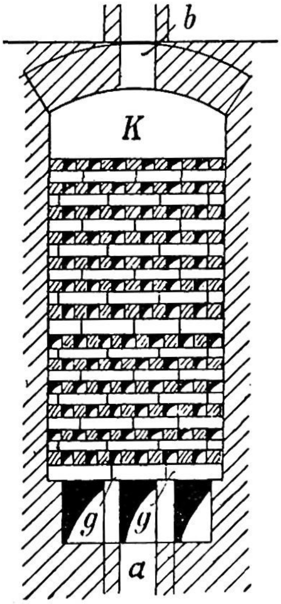

Fig. 59.—Regenerator.

As already noted, air regeneration is most effective when applied to gas-fired or partially gas-fired kilns, the latter type being shown in fig. 60. In this case the kiln is one of the Mendheim type, with a gas producer (k, k) of such construction that the firing can be started with wickets in the ordinary manner, and when the fuel is fully alight and more rapid heating can be safely used, the depth of fuel on the grates of the producer is increased from a few inches to 2½ to 3 feet, and so becomes a gas-producer instead of an ordinary fire-box. At the same time, heated air is supplied to the combustion chamber through the regenerator of a neighbouring kiln, or from a kiln which is cooling, until the one actually under fire is capable of supplying itself with a sufficiency of hot air.

It will readily be seen that this arrangement can only be effectively used where a number of kilns (at least three) are close together, and should the output of the works necessitate the continuous employment of several kilns, some such arrangement may effect considerable economies in fuel.

In cases where it is found difficult to make the fire burn properly in passing from the "ordinary" to the "producer" stage, the insertion of a steam pipe of exceedingly small bore to blow a current of air through the fuel in the producer will enable the change to be effected without difficulty. The steam used is so small in amount, and it is so completely destroyed in passing through the fuel, that no danger to the goods in the kiln can ensue; its use can be stopped as soon as the producer is in full working order, and be re-started for a short time whenever a stronger fire cannot readily be obtained.

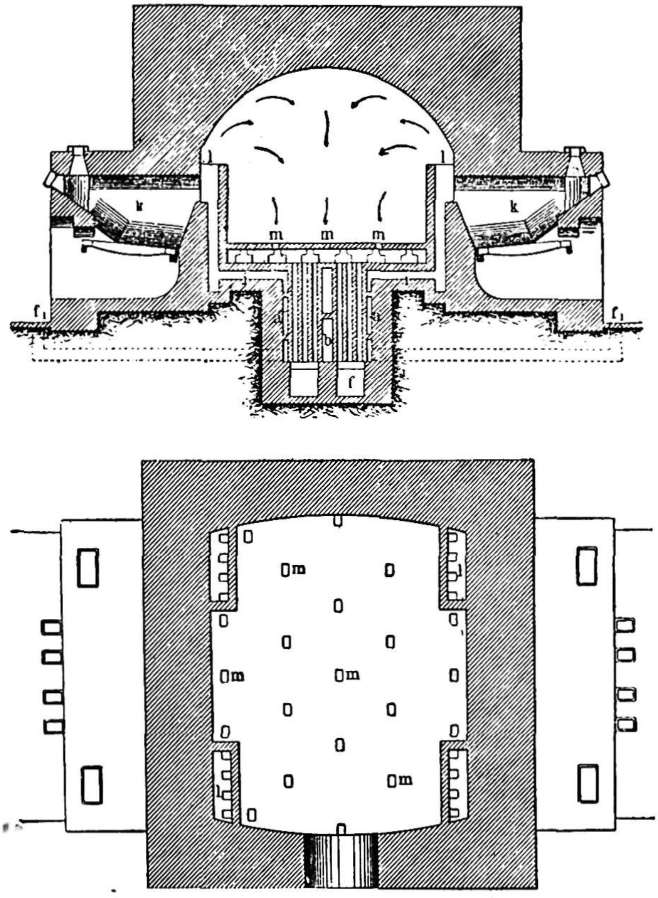

FIG. 60.—Down-draught kiln with regenerator (*after B. Kerl*).

An arrangement of the kind illustrated requires more fuel than a kiln fired exclusively by gas, but it is far more economical than a single coal-fired kiln, and the heat obtained is much more easily regulated. Moreover, the alterations involved are neither complicated nor costly in most cases, as the position of the regenerators can be varied to suit the needs of particular circumstances, though, naturally, the nearer they are to the kiln itself the more effective will be the service they render.

Horizontal-draught kilns (fig. 61) are known in this country as Newcastle kilns. They consist of a long, rectangular chamber capable of holding 8000 to 20,000 bricks. The smaller ones have three fires at one end and a chimney at the other, but in the larger ones the fires are at both ends, and a chimney is placed in the centre of each side wall. The fire-gases enter from the fire-places and travel horizontally to the chimney flue and thence up the chimney; consequently, the longer the kiln, the more advantageously will the heat be used. Unfortunately, if a kiln of this type is more than about 25 feet long the gases will have cooled to such an extent that some of the goods will be insufficiently fired, whilst those at the front of the kiln will be overheated. Consequently, a large amount of heat is wasted in kilns of this type. Notwithstanding this important objection, Newcastle kilns are among those most extensively used in the firebrick trade, particularly in Northumberland, Durham, and Scotland.

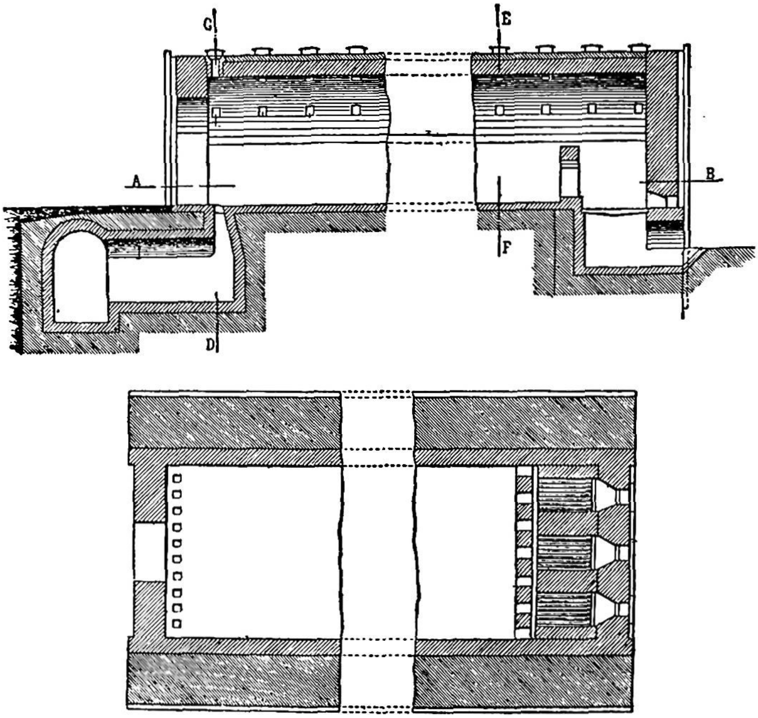

FIG. 61.—Newcastle kiln.

A great saving may be effected by connecting several Newcastle kilns together and passing the fire-gases through them in succession, but by far the best means is to use a continuous kiln.

Continuous kilns were first patented by Hoffmann in 1858 for burning building bricks, but since that time they have been modified in several respects without destroying the essential principle, and are now perfectly satisfactory for burning firebricks and other refractory goods. The chief alterations consist in substituting grates or fireplaces for the pillar arrangement used by Hoffmann, and in erecting permanent partitions which divide the kiln into a definite number of chambers. It is advisable to leave plenty of holes in the lower part of the partition for the gases from the previous chamber to pass into the fire-box of the succeeding one. These fire-boxes then impart a strong upward tendency to the stream of gases which, being drawn from near the bottom of each chamber, has a much better chance of being diffused throughout the entire space than when the direction of the gases is more horizontal. In some forms of this class of kiln, the bottom is perforated and the gases are led beneath the partition instead of through it to the fire-box of the next kiln, after having been mixed with a certain proportion of fresh (heated) air in order to maintain proper combustion.

In the " Belgian " kiln, a grate in each chamber runs across the whole width of the tunnel; in the Brown and Guthrie kilns, a trough occupies the same position, and is equally satisfactory in most cases. The " Belgian " continuous kilns built by Messrs. W. Jones & Sons have been used satisfactorily by a number of works for several years for burning fireclay and silica bricks. In a Scotch works, one of these kilns uses an average of 6 cwt. of coal for burning one thousand bricks at Cone 14 (1410° C.), the draught being produced by an electrically driven fan using 7 units of current per hour. At one of the Stourbridge works, 2 cwt. of small coal is used for each ton of goods burned in their " Belgian " kiln at Cone 5*a* (1180° C.).

It is sometimes stated that " the ordinary continuous kiln is quite unsuitable for burning firebricks." This is quite true, but the " ordinary " continuous kiln must not be confused with the ones described in this and the following pages.

Unless it is divided by partitions into chambers, and special provision is made for working these independently of each other, a continuous kiln is of little value to most manufacturers of firebricks. A chamber kiln properly designed and suitably constructed for firebricks is, however, far superior to separate kilns, giving better bricks and saving two-thirds of the coal. The reason that several firebrick manufacturers have found continuous kilns to be unsuitable is that they have not chosen one of the right kind.

The general direction of the draught is horizontal, and the fire-gases pass from one chamber to another until their further use is undesirable; after this they pass into the main flue and away to the chimney. The heated goods are cooled by means of a current of air which is thus heated regeneratively and is used for the combustion of the fuel. A further supply of hot air is obtained by means of flues in the brickwork of the kilns. The arrangement of these flues is a matter of great importance and has been made the subject of numerous patents. Instead of describing these,[1] the author deems it preferable to take one kiln as typical of the best that has yet been done in this direction, viz., the " *Staffordshire* " *kiln*,[2] patented by Dean and Hetherington, which must not be confused with the ordinary pottery kiln used in North Staffordshire, although such mistake is natural, considering its title.

The general form and construction of the " Staffordshire " kiln closely resemble those of a Hoffmann kiln of similar capacity, the improvements

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[1] They are described and illustrated in the author's *Kilns and Kiln Building* (Clay-worker Press, 43 Essex Street, W.C.).

[2] It must be clearly understood that the author has no financial interest whatever in this or any other kiln.

consisting in the addition of grates, hot-air flues, and partition walls.

In the "Staffordshire" kiln the means of supplying hot and cold air to different parts of the kiln are unusually complete and, as only one face of fire is used in each chamber, this kiln is capable, under good management, of giving results equal to the best down-draught kilns, with coal consumption as small as in continuous kilns. This is brought about by the construction, in a continuous kiln, of damper-controlled passages leading from the outer air to the flues under the fire-grates in the bottom of the kiln in each chamber, as shown in figs. 62 and 63, and of similar flues leading from the hot-air flues and from the outer air in such a way that, by appropriate connections, air of any desired temperature and of any desired volume may be admitted to any part of the kiln.

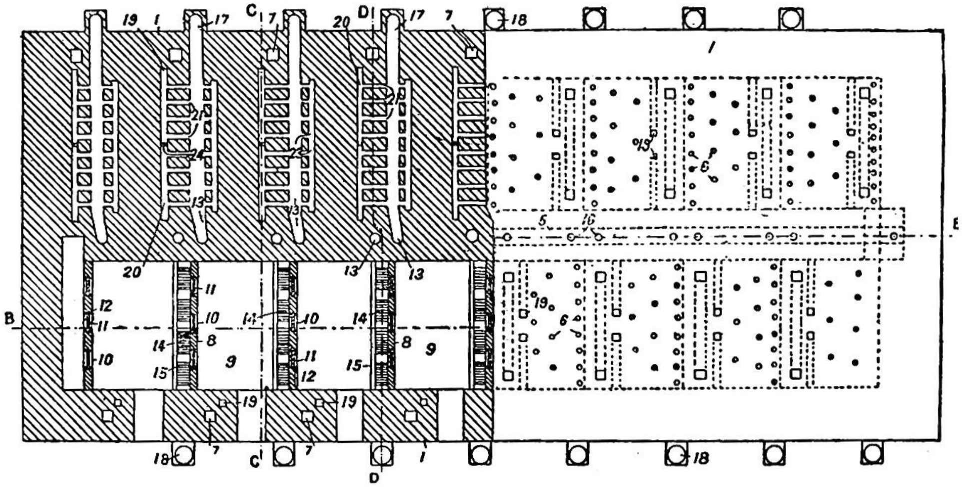

FIG. 62.—Plan of "Staffordshire" kiln.

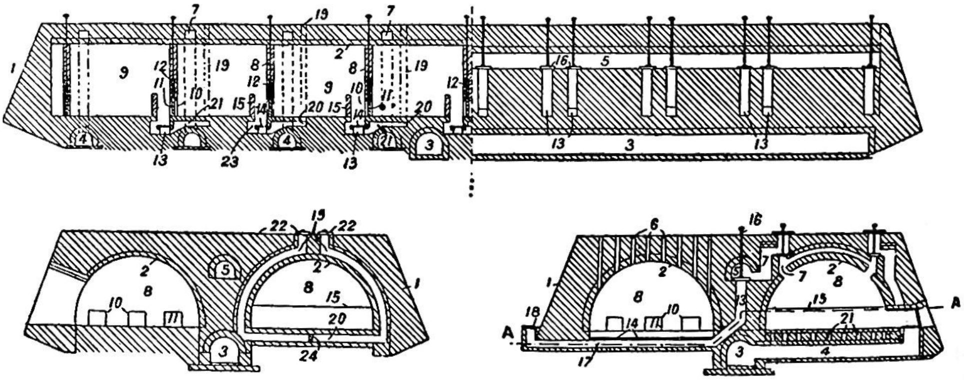

FIG. 63.—Sectional views of "Staffordshire" kiln.

By suitably working the dampers shown in figs. 62 and 63, the following results may be obtained :—

(*a*) By opening dampers 11 and 18 the whole or part of the hot air from the finishing or cooling chambers may be admitted to the chambers containing the freshly set bricks, and the steam resulting from the heating of these goods led away from the top through flues 7 and 3 to the chimney.

(*b*) By opening the dampers (16) of the flue (13), hot air from flue 5 may be led under the grates (14) to develop the highest possible temperature in the finishing chamber, or to distribute hot air uniformly from the hot-air flue (5) to a chamber containing green goods.

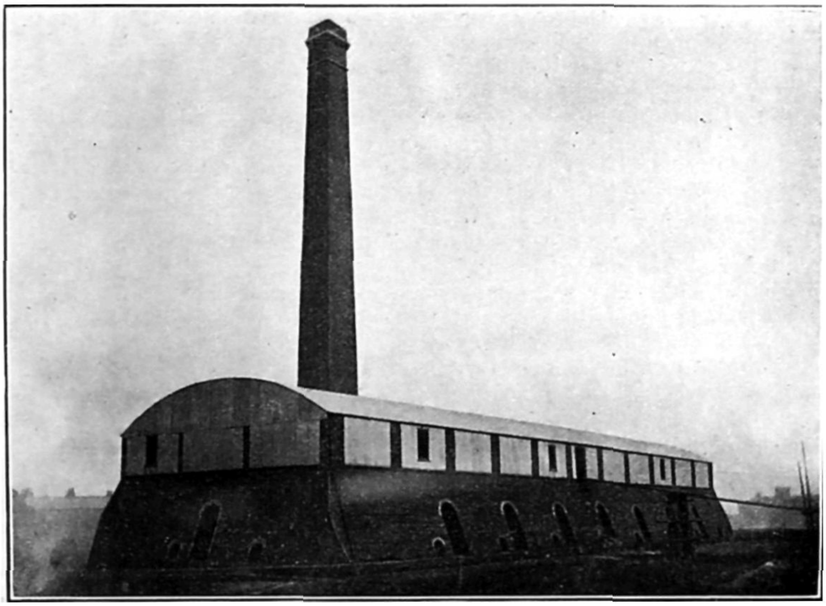

FIG. 64.—" Staffordshire " continuous kiln.

(*c*) The admission of cold air to a cooling chamber is kept under perfect control by means of dampers (18) and flues (17).

(*d*) The temperature of the hot air entering a hot chamber from one that is cooling may be perfectly regulated by the admission of air through flues (17) and (19).

(*e*) The volume of air admitted through the various flues allows of the accurate adjustment for reducing and oxidising atmospheres.

(*f*) The fire and hot gases may pass from chamber to chamber through openings (10), whilst cold air only is admitted to the underside of the grates (14) through flues (17).

(*g*) Any chamber can be completely sealed by closing all the dampers, thus allowing a good annealing.

Gas-fired continuous kilns have been known for many years, James Dunnachie having erected one at Glenboig in the year 1881 ; yet many attempts have been made to apply gas to kilns which have resulted in disastrous failures.

Two principal reasons for these failures may be given: those attempting to use gas did not know how to burn it and did not permit it to enter the kiln at the proper point. Subsidiary failures have been due to attempting to use cold instead of hot air for mixing with the gas and other equally impracticable ideas, the result of ignorance of the characteristics of the gas used.

It is generally thought that gas-fired kilns are difficult to manage and that they effect an enormous economy in fuel. Neither of these ideas is correct. A properly constructed gas-fired kiln is quite easy to manage—the difficulty lies in the design and not in the manipulation—and the fuel consumption is rather more than that of any equally well-designed coal-fired continuous kiln.

The real advantages of gas are its greater cleanliness, the better colour obtained on the goods, greater regularity of heating, and, above all, the higher finishing temperature which can be reached when gas is used. This last is of the greatest importance in firebrick manufacture, though few British makers of refractory goods realise this fact.

The Dunnachie kiln has been chiefly used in connection with firebrick burning, though well adapted for ordinary bricks; but it has not been the policy of the inventor to encourage the erection of similar kilns in this country or in Scotland, and consequently the kiln, though well known by name, is not familiar to more than a few privileged workers as regards its constructional details. Abroad (where the possibility of competition does not exist) a number of Dunnachie kilns have been built, and, when the original design has been closely followed, have proved quite successful and economical.

It is, indeed, only to be regretted that more do not exist in this country. The Dunnachie kiln has a solid floor, thereby overcoming one of the greatest disadvantages of the Mendheim gas-fired kiln, and the larger flues give a more satisfactory control as well as a more rapid burning of the goods, and at the same time are much less easily choked.

The gas-producer used may be of any type supplying gas at a pressure of about one-hundredth of an atmosphere (4-inch water column), though at Glenboig, Wilson producers were used for the original Dunnachie kiln.

The Dunnachie kiln presents a very different appearance to the ordinary continuous kiln because of the great distance between the two rows of chambers. In the ordinary coal-fired continuous kilns, with sixteen chambers, twelve are placed back to back, close together, and the remaining four are placed two at each end of the others, so as to form a complete "ring." In the Dunnachie kiln (figs. 65 and 66), on the other hand, there are only ten chambers, placed in two rows of five, and with a space of 20 feet between them, the chambers at the end of each row being connected by underground flues. In the centre of this 20-foot space the gas valves are arranged, and, if roofed in, the space forms a convenient room for drying goods, being kept warm by the heat radiated from the ends of the chambers. Some heat which would otherwise be lost is made use of by this arrangement of the kilns, to the general advantage of the works. If desired, the space above the kilns may also be roofed in, and used as a making and drying floor—a custom particularly common with continuous kilns in Germany, but not so popular in Great Britain.

The chambers used at Glenboig have a capacity of about 18,000 bricks, and measure 17 feet by 10½ feet by 10½ feet internally, and, worked at ordinary speed, can produce an average output of 400,000 firebricks a month.

The chimney is placed at one end of the structure, the main flue leading to it being placed around the sides, as shown in fig. 65. This plan necessitates some loss of heat in the main flue, but as the gases passing through it are at a comparatively low temperature, this is not considered to be of much importance, especially as the chimney draught can be accelerated to any required extent by means of a fan. It is certainly better that the heat should be lost from the main chimney flue rather than from the flues conveying hot gas to the kilns, which seems to be the only other alternative if the present simplicity of arrangement and accessibility of flues are to be maintained. Under such conditions a blower may be used instead of, or in addition to, the chimney or fan draught; but this requires care, or its use may become dangerous.

"Steaming" or "smoking" of the goods is effectually carried out by burning a small quantity of gas mixed with an abundance of cold air in the chambers to be smoked, or, if there is a sufficient supply, hot air from the cooling chambers is used. During this "steaming," openings in the arched roof of the chambers (corresponding to the "feed-holes" in the ordinary kiln of the Hoffmann type) and the ports near the floor level of the kiln are kept open until the whole of the steam has been removed, and the goods are distinctly hot; they are then closed.

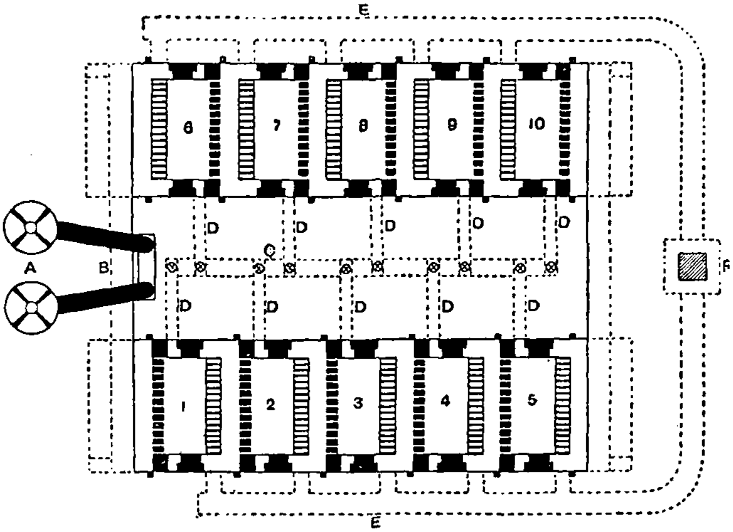

FIG. 65.—Horizontal section of Dunnachie's gas-fired kiln.

The burning then commences by admitting gas at a temperature of about 300° C. from the producers through valves C (fig. 65) into flues A and subflues B (fig. 66), in the top of which are openings for the gas to escape, hot air for the combustion of the gas being supplied at the same time from the chamber which has just finished firing. It is the employment of the heat in the finished goods for heating the air required for the combustion of the gas which constitutes the principal feature of the Dunnachie kiln, and is the chief cause of its success. This kiln was, in fact, the first in this country to combine the advantages gained by the use of gas as fuel with the "regeneration" of the air used for its combustion by means of the waste heat from the burned-off chambers. This principle of heat regeneration has been recognised for nearly a hundred years, and was applied with remarkable success in 1856 to the melting of steel by the late Sir F. Siemens, but the credit of its successful application to the requirements of the clay industry must be given to Mr. James Dunnachie, who first employed it in the kiln now under consideration. For its application to *single* kilns see fig. 58.

The air is heated in a manner very similar to that now employed in most continuous kilns using coal, by drawing it through the chambers containing finished goods which are still very hot (in the case of firebricks of best quality the air is heated to a " blue-white heat " before it comes into contact with the gaseous fuel). It is conveyed from one chamber to another by openings D (fig. 66) in the floor of the chambers leading to a flue C, next through slits in the brickwork to another flue, and thence through openings in the arched roof of this latter flue into a smaller one, from which it passes at, or slightly below, the floor level of the kiln into the next chamber by means of a series of openings, the size of which is calculated so as to supply the correct proportion of air to the gas. (Usually the capacity of the air-openings is two and a half times that of the gas.) As these air-openings extend the whole length of the chamber, even heating is thereby effected.

The gas catches fire where it comes into contact with the air a little below the floor level, and for some distance above it, the flame rising a considerable height in the chamber in huge sheets of a clear bright colour, and practically free from smoke if the air and gas are in the correct proportions. The products of combustion then pass through the following chambers, heating the bricks in them, until the heat left in the gases is so small as to be of little value, when they are turned into the main flue leading to the chimney.

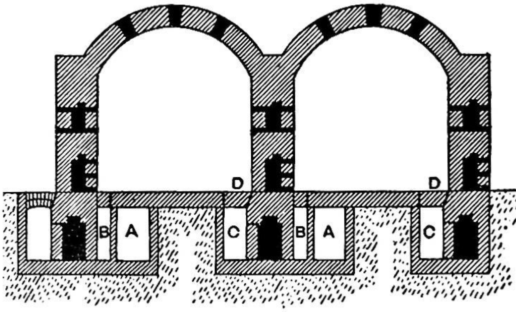

FIG. 66.—Vertical section of Dunnachie's gas-fired kiln.

If, for any reason, a supply of air is required at a higher level than the floor of the kiln, it can be supplied by opening dampers in other flues (fig. 66), which are so arranged as to supply hot air from the preceding chambers, or, by opening dampers at their ends, cold air can be supplied in any desired amount to the chambers. These flues are not generally required unless the firing in the burning chamber is not hot enough, or when the chamber is too hot and cold air must be supplied to prevent the bricks melting.

All these air- and gas-flues are controlled by dampers and valves of a simple character, and the supply of hot or cold air and gas can be regulated with the greatest nicety to the changing conditions of the kiln.

The " round of the kiln " when burning firebricks is somewhat as follows :—

No. 1 chamber—being emptied. No. 2 chamber—open and cooling. No. 3 chamber—red hot, being cooled by air supplied through a flue at its base and carried on to No. 4 chamber. No. 4 chamber—white hot, being cooled by air from No. 3, which is passed on to No. 5. No. 5 chamber—in full fire for thirty-six to forty-eight hours, being supplied with hot gas from the producers, and with "white-hot" air from No. 4. No. 6 chamber—very hot, being heated by products of combustion from No. 5. No. 7 chamber—heating up to red heat by gases from No. 6. No. 8 chamber—steaming for forty-eight hours; filled with green bricks. No. 9 chamber—filling with green bricks. No. 10 chamber—empty, ready for filling.

The cooling of each chamber takes about seventy-two hours, though varying with the nature of the goods. It can be accelerated by a blast of cold air blown into the top of the chamber during the last day of the cooling. The hot air thus obtained may be used for the kiln, any excess being employed for heating drying sheds, etc.

The *Shaw* kiln so closely resembles the Dunnachie kiln that a very careful and detailed comparison of both is needed before the differences can be distinguished. The chief advantage of the Shaw kiln lies in part of the flames passing beneath the floor of each chamber, thus making the latter hotter than in the Dunnachie kiln and so ensuring a more uniform temperature throughout the chamber.

The continuous kiln patented by G. Mendheim (figs. 67 to 70) is extensively used on the Continent. In this the gas enters at the four corners of each chamber and rises up the bag-walls; the products of combustion then pass out through a central opening in the floor, which delivers them to the bags of the next chamber or to the main flue. This arrangement has the advantage of using a minimum number of dampers, and enables the supply of gas to each half of the burner to be controlled independently. The pipes (g, g) may have as many branches (p, p, q, q) as desired. The gas passing out of these branches meets hot secondary air from the previous chamber, through the flue l, and the flame rises up through the bag s, and after heating the goods in the chamber it passes through the perforated floor and thence either to the next-chamber or to the chimney, as may be desired. Smoke or hot-air flues can be fitted to this kiln if desired; they do not in any way interfere with its general action. The construction of Mendheim's burner is shown in fig. 71. As shown in fig. 68, there are four flues to carry the waste gases under the floor of each chamber.

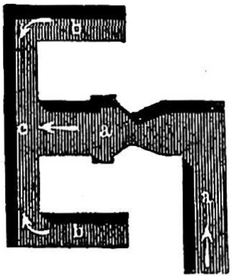

Fig. 71.—Plan of Mendheim's burner (*after Kerl*).

When materials are to be burned at a very high temperature it is often desirable to avoid the use of a perforated sole in the kiln, and under such conditions the use of a modification of Mendheim's kiln (shown in fig. 72) is advantageous. In this kiln, the producer gas enters through the flue g, which divides into four subsidiary flues, g_1, g_2, g_3, g_4, which discharge their contents into the four corners of the chamber to be heated. In these corner-burners the gas is mixed with the requisite quantity of air and is burned, the flames rising vertically to the top of the chamber and then passing downwards through the goods, and out through the well c into the flue d, and the branch flues d_1, d_2, d_3, d_4, by means of which the flue gases enter the next chamber. The well-hole c also has a direct connection to the main flue R by means of the short flue f, this being controlled by a damper. By this means, a single damper suffices to shut off any chamber, when it is required to do so.

Numerous other designs of gas-fired chamber kilns have been placed before the public, but most of them have not been proved to be of value, and so need not be considered here.

There is undoubtedly a great opening for the further application of gas to the burning of all kinds of firebricks; and the success which has attended the Dunnachie and Mendheim kilns ever since their introduction should give brickmakers an incentive to adapt their own kilns as far as possible, or to seriously consider the advisability of erecting fresh ones to be fired exclusively with gas. The reason why most firms are afraid to make the change is that they have heard or read of numerous and expensive failures to apply the gas properly to the kilns—due, as already explained, to the belief that it should be introduced near the top of the chambers—and are afraid to risk their own capital in a similar venture. This is bad business, because it is looking at the subject from one side only instead of regarding it from every point of view. The fact that some kiln-builders recommend a certain class of kiln is not by any means conclusive evidence that the facts which tell against their own invention are fairly represented. This is where the advice of an entirely independent expert is valuable, provided that he is really independent.

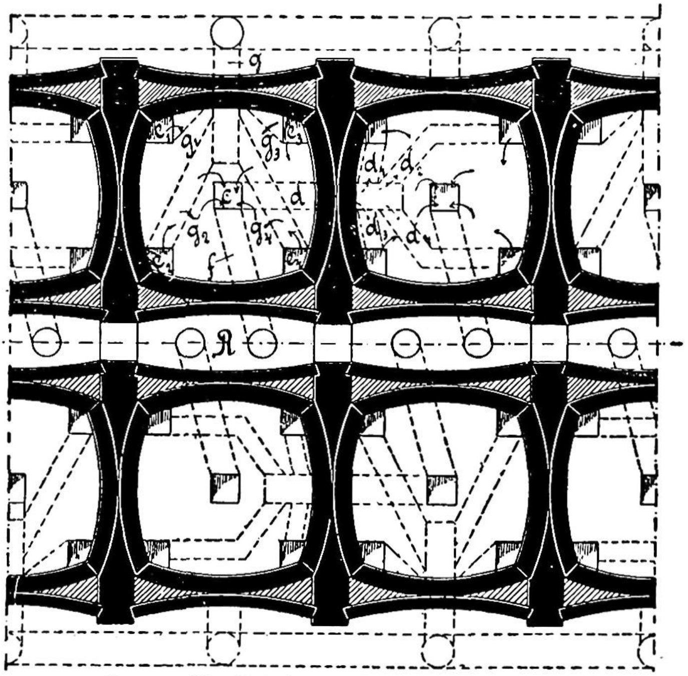

FIG. 72.—Mendheim's kiln for highest temperatures.

The success which has been obtained in the adaptation of gas to the firing of single kilns is drawing considerable attention to the subject of gas-firing, and the general application of this fuel to the firing of refractory goods is only a matter of time.

The construction of gas-producers requires special knowledge, and should not be attempted by the brickmaker except under reliable supervision. The general principles involved can be learned from books[1] on the subject, but practical experience is essential.

The use of a gas-producer requires a slight training, though when this has been obtained the work is far easier than the ordinary stoking of kilns, and the temperature in the latter can be far more accurately and easily regulated.

Tunnel kilns, in which the fires are near the centre of a long tunnel, are

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[1] As, for instance, the one mentioned at the foot of p. 294.

sometimes used for burning firebricks. The bricks travel on trucks, the lower part of which, being of metal, must be protected from the heat, whilst the upper part is made of fireclay slabs. On their journey through the tunnel the bricks are first warmed by the escaping gases and gradually pass into the hottest part of the kiln. Continuing their journey, they pass through a further length of tunnel, in which they are cooled by a current of air which is afterwards used for the combustion of the fuel.

One of the most successful types of tunnel kilns used for burning firebricks in this country consists of a plain brickwork tunnel about 300 feet long, of which 150 feet form the preheating zone, 36 feet the firing zone (comprising eleven gas-burners on each side of the kiln), and 114 feet the cooling zone. A current of air and the hot gases produced by the combustion pass through the tunnel in the opposite direction to the goods, so that the greatest possible use is made of the fuel and of the heat in the cooling bricks. Each car or truck carries about 700 bricks, and passes through the kiln at the rate of 5 feet per hour. The metal parts of the cars are protected from the action of the hot gases by a firebrick bed on top of the cars, and by a sand-seal on each side of the cars in the tunnel.

A coal-fired tunnel kiln which has been successfully used in the United States is the Didier-March kiln (fig. 73), which is similar to the kiln just described, but has four fireplaces instead of a producer and gas-burners. The arrangement for the circulation of the air- and flue-gases in this kiln is based on that of the Faugeron tunnel kiln, which has been largely used for pottery manufacture in France. Other "open type" tunnel kilns, also in use for burning firebricks in the United States and elsewhere, differ only in small details; of these the ones most suitable for firebricks and other refractory materials are the Marlow, Owen, Zwermann-Russell, Gibbons, and Harrop tunnel kilns, respectively.

Where the temperature need not exceed 1350° C., and protection of the goods from direct contact with flame is considered important, there are many advantages in using a Dressler tunnel kiln, which was patented in 1910, and has been subject to various improvements in later years. In the tunnel of this kiln (fig. 74) are tubular heating chambers which extend from the hottest part of the kiln to the inlet, the portion of the tubes in the heating zone being made of carborundum or other refractory material, whilst in the greater part of the preheating zone they are made of metal. In these tubes, a mixture of producer gas and air is burned, the heat from which is radiated from the thin walls of the tubes into the tunnel. The gases from the burning fuel are drawn along the tubular combustion chambers by means of a suction fan, so that the interior of the chambers is always at a rather lower pressure than that of the tunnel, thus effectively preventing the escape of fire-gases through any leaks in the thin walls of the combustion chambers. The air immediately surrounding these chambers is heated and thereby caused to circulate around the goods to be burned and around the combustion chambers, as shown in fig. 75, the temperature of the interior walls of the kiln rising progressively from the inlet to the hottest part, so that as the goods pass along the tunnel they become more and more heated, until finally the firing is completed near the centre of the tunnel; as the goods pass still further along they are cooled by air circulating around similar pipes, through which a current of cold air is passed. Some of the hot air from these tubes is used for the combustion of the gas used as a fuel, and the remainder is available for drying other goods.

The goods are placed on cars as in other tunnel kilns and passed through the tunnel, no sand-troughs or other lutes being required, as the lower part of the cars is not heated by the circulating gases.

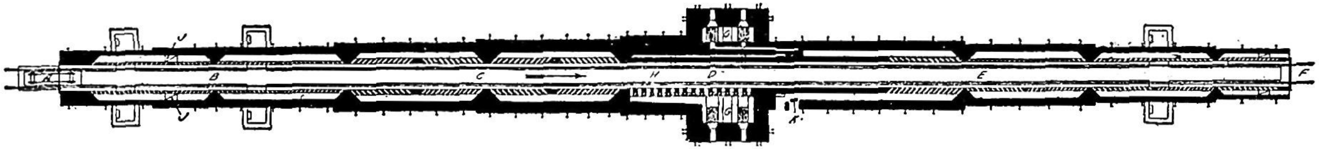

FIG. 73.—Diagrammatic plan of Didier-March tunnel kiln.

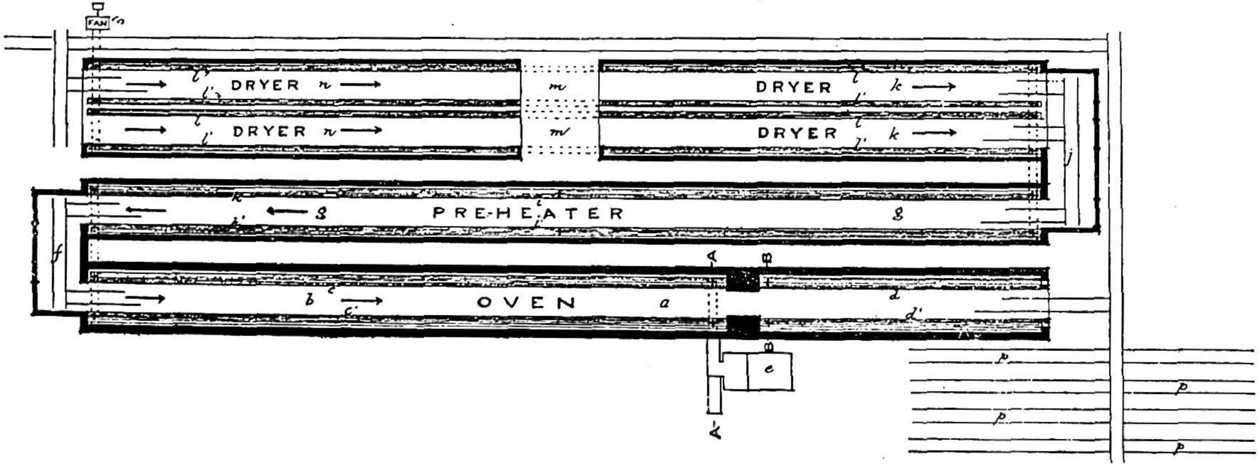

FIG. 74.—Plan of Dressler's tunnel kiln with pre-heater.

The Dressler tunnel kiln is now being used very successfully in Ohio, U.S.A., for burning blocks, etc., for use in melting glass. The finishing temperature is Cone 11 (1350° C.), but unless it is specially important to protect the goods from direct flame, an "open" tunnel kiln is in every way preferable to a "muffled" one.

A properly designed tunnel kiln has the following advantages when the output is sufficiently large to maintain it constantly in full work; it is useless for small and irregular outputs:—

(i) The heat is utilised to the utmost, provided the tunnel is sufficiently long and is well managed.

(ii) The goods are automatically carried forward in the tunnel at a constant speed, and the time required for burning is greatly reduced.

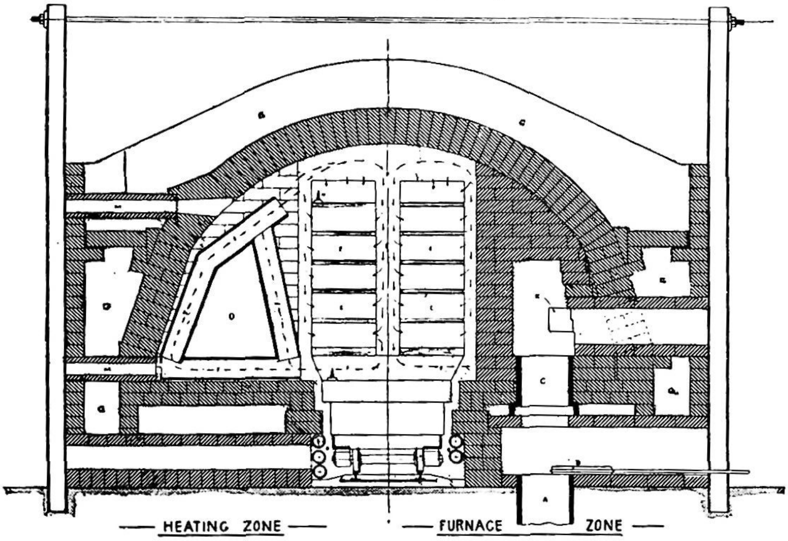

FIG. 75.—The Dressler tunnel oven.

(iii) The temperature at each part of the kiln remains quite constant, and can be readily controlled. At the same time, the finishing temperature may be altered at will, so that goods requiring different finishing temperatures may be readily fired in the kiln.

(iv) The kiln does not require to be cooled down before the next lot of goods are fired, as in the ordinary single kiln, nor is the brickwork heated and cooled alternately, as in a Hoffmann kiln or continuous chamber kiln.

(v) The zone of greatest heat is confined to one part of the kiln, so that firebricks of the best quality are only required in this part of the tunnel; this effects a great saving in construction and in renewals.

(vi) The cost of repairs is reduced because no part of the kiln is subjected to alternate heating and cooling.

(vii) Much labour is saved in setting and drawing the goods, as it is both quicker and easier to place them on cars in a long shed than in a hot and often dark kiln.

For some classes of refractory ware, such as chemical porcelain, the Dressler tunnel kiln, or a simple modification of it, is highly advantageous, as it does away with the use of saggers and all their disadvantages. Tunnel kilns of various types are being increasingly used for all kinds of refractory articles with great success. Where they have failed, the failure is almost invariably due to—

(*a*) The various zones being too short.

(*b*) The goods being passed too rapidly through the tunnel.

(*c*) The gas-burners or fires being badly managed.

Of these three sources of difficulty, the first is usually the most important, as very long tunnel kilns are costly, and attempts at economy are usually made in the direction of reducing the length of the tunnel.

Continuous kilns—of whatever type, and whether gas- or coal-fired—can only be worked satisfactorily when the output is sufficiently large to keep the kiln fully employed. For smaller or irregular outputs, or where there is great variety in the goods to be burned, single kilns are preferable. Gas-fired kilns are more economical and give a better product than intermittent coal-fired kilns, but in continuous kilns the difference in the amount of fuel used with gas- and coal-firing is not marked, as, if the coal-fired kiln is properly designed, the coal is really gasified quite as effectively as in a producer. In such a kiln, the greater economy in gas-firing could only be found in such directions as a reduction in labour of wheeling the coal, the greater durability of the kiln, or the smaller amount of spoiled goods.

A frequent cause of dissatisfaction with continuous kilns used for burning refractory clays is the non-realisation of the importance of leakage due to defective masonry both in the kiln walls and in the flues. A certain amount of leakage must occur with all kilns, but when working "continuously" this must be kept to the lowest amount, or it will be impossible to realise the expected temperatures. In an intermittent kiln, leakage, though wasteful, is of secondary importance, as each kiln is independent of the rest, but when connected chambers are used it will be found that air leaking into the kiln through defective walls or flues will cause serious trouble to the fireman, preventing him from obtaining the requisite draught.

Leakage can only be detected with certainty by keeping a continuous record of the air-pressure (draught) within the kiln at those points where firing is being carried on, and for this purpose a *recording draught gauge* (fig. 76) is necessary. These instruments have not met with the reception they deserve, for several reasons; one of the most important being the opposition of the firemen, who regard them as undesirable because they infallibly show any neglect and irregularity on their part. Yet such gauges are of real value to the fireman who will take the trouble to overcome his prejudice against them, and they will not only lighten his labours, but will save him many hours of anxious thought when things are not going as they should do owing to an adverse wind, an undiscovered crack in the walls, or some other cause of defective burning. An attachment can be added, if required, whereby an electric bell is rung when the interval between the two baitings exceeds a pre-arranged time, so that a foreman or manager can be warned if the burner neglects his duty. The constant use of these charts has an excellent effect on burners who are inclined to be careless. Incidentally, they also show the serious effect of the weather on the burning of kilns with chimneys, as compared with the steady draught induced by a fan.

In carrying out investigations with a view to reducing the amount of fuel burned, or to increase the firing temperature without using more fuel, the employment of a draught gauge is more important than the use of a pyrometer, for the latter will only indicate the temperatures reached, whilst the former indicates, by variations in the draught, many of the reasons why the temperature varies at different stages of the firing. Such a study of draught variations is invaluable to the manufacturer of high-grade refractory goods, as it is in these apparently small matters that he is enabled to improve the quality of his wares, as well as to see the directions in which he may most probably economise in time, labour, and fuel.

Muffle kilns are seldom required in the manufacture of refractory goods. They are made by building an inner chamber in one of the kilns previously described, this inner chamber or muffle being so arranged that the kiln-gases circulate around the chamber but are unable to enter it directly.[1] Various types are used in different works, including single muffle kilns, continuous muffles, and muffled tunnel kilns. They are chiefly employed for large goods which cannot be placed in saggers or in ordinary "open kilns," because it is important that the goods should not be stained by fire-gases.

Alexander Wright & Co., Ltd., Westminster.

FIG. 76.—Recording draught gauge.

Selecting a Kiln.—For refractory goods of the very highest qualities and requiring to be burned at the highest temperatures obtainable industrially, it is essential to use single gas-fired kilns of small size, preferably with a regenerator, so as to supply hot air.

For larger quantities of goods burned at somewhat lower temperatures, a tunnel kiln or a chamber kiln on the continuous principle (not a Hoffmann kiln) is preferable. Such kilns are not extensively used, however, because it is necessary to keep them uniformly supplied with a large quantity of goods of a similar character. Most continuous chamber kilns, otherwise suitable

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[1] A considerable amount of gases will pass through the walls of a muffle unless these are glazed internally, but in most cases the gases which do pass through the muffle are harmless to the goods to be burned. In any case, the muffle acts as an effective filter which keeps off the flame and coarser particles of dust and imperfectly burned fuel, and so efficiently protects its contents.

for the purpose, are much too large for the commercial requirements of manufacturers of refractory goods. By retaining the present length and height of the chambers and reducing the width to half or to two-thirds the usual dimensions, this type of kiln would be made much more valuable, as the excessive output would be reduced without in any way affecting the economical properties of the kiln.

The principal matters to be considered in the selection of a kiln for any particular type of refractory articles are—

(i) *The first cost,* which depends largely on the output required, a kiln for a small output costing more in proportion to its output than a larger one. Apart from this, it is not desirable to have a kiln built as cheaply as possible, because although its first cost may be low, the amount of heat lost by radiation and the repairs required to keep the kiln in fair working order will more than counterbalance the difference in first cost between a cheap kiln and one which is thoroughly well built, so that the apparently cheap kiln will eventually prove to be the more expensive one. Many manufacturers are very prone to attempt unwise economies in the first cost of kilns, by having only thin walls, omitting the use of insulating bricks, using poor foundations and rubble for filling instead of insisting upon brickwork throughout. Such practices are very foolish, as the kilns will be more than correspondingly expensive in other ways, as shown below.

In a similar way, an attempt is sometimes made to save money by building a chimney which is only just large enough for the work. This is really a false economy, as sooner or later it will result in the gases being turned into the chimney at too high a temperature, and consequently any saving on the original cost of the stack will be far more than counterbalanced by the unnecessarily large amount of fuel used in firing the kiln. Here, again, the chimney must be regarded as a capital expense, and the saving effected by its use must be reckoned as legitimate interest on the capital spent. If a short chimney is erected, the fuel wasted by turning hot gases into the chimney will represent an annual expenditure corresponding to, possibly, 25 per cent. interest on the additional amount of money originally required to have made the chimney the right size. Not only so, but with ample capacity (in other words, with ample draught) it is possible to burn the bricks far more effectively, and so not only to increase the output of the kiln, but to turn out a better class of goods, and consequently to produce a larger income for the same amount of expenditure.

(ii) The *size of the kiln* must be equal to the average output, or a trifle larger, as it is better to miss a little trade in the best years than to be saddled with too large a kiln during bad seasons. The question whether it is better to have two moderate-sized continuous chamber kilns or one single one of equal capacity is one which admits of much discussion, though the actual loss of working a large kiln partially is less than working a small kiln fully, and keeping another of equal size idle except for occasional use. Owing to the alternate heating and cooling to which they are subjected, kilns do not resist the action of weather well when out of use for a long time. Hence, it is better to have one large rather than two smaller continuous kilns, but this should not be much larger than the average output of the works for a period extending over several years, if the best results are to be obtained.

For works of moderate size, in which there is not sufficient output even for a reduced continuous kiln, as suggested, the down-draught and Newcastle kilns are satisfactory. Round down-draught kilns give the most uniform heating of all single kilns, and they are cheaper to build than rectangular down-draught kilns. On the other hand, they are more difficult to set, so that there is really little to choose between the two shapes. If possible, these kilns should be connected, either to each other or to a central regenerator, so as to reduce the wastage of hot gases by employing it in a dryer or another kiln.

(iii) The *heating power* of a kiln is perhaps its most important feature, for if a kiln cannot raise the goods to the required temperature, or maintain them at that temperature, all its claims are useless. The heating power of a kiln is chiefly dependent on (*a*) the amount of heat that can enter the kiln at once, and (*b*) the amount of heat lost by radiation or by useless brickwork. The amount of heat admitted depends on the draught and, therefore, on the size of the flues and the number of obstructions placed in the path of the hot gases. Consequently, a kiln with large flues and few " turnings " will give a much better heating effect than another kiln of the same size with smaller flues and numerous obstructions. The loss of heat in a kiln is chiefly due to the walls being too thin, or actually leaky, and to wet foundations. For these reasons, it is well worth while to secure a good set of plans of a well-designed kiln than a cheaper set supplied by some second-rate builder. The foundations of a kiln must be of such a nature as to keep the kiln and the flues quite dry, so that a good impervious foundation should be built even if the cost of the kiln is thereby greatly increased. Some firms, when erecting a kiln, adopt the foolish policy of comparing only the various types of kilns and pay no heed to the foundations. Indeed, they grudge the money on these accessories as being largely wasted. Yet a comparison of the results of kilns with and without good foundations will, if thoroughly made, soon show any fair-minded man the great advantages of a good foundation and a rainproof roof, and the serious losses which will be incurred if these are omitted.

(iv) The *cost of repairs* must be taken into consideration, and the type, design, and construction of the kiln so arranged that the cost of repairs will be as low as possible. Otherwise, what appears to be a cheap kiln may prove to be very expensive.

(v) The *fuel consumption* is very important, and the kiln which is most economical in this respect should be chosen, provided the saving in fuel is not counterbalanced by losses in other ways. If a kiln is to have a minimum fuel consumption, it must have: (*a*) Thick walls and crown which do not permit the escape of much heat or the admission of cold air through leaks in the structure. The use of highly porous diatomite bricks as heat-insulators is advantageous, and enables thinner walls to be used. The heat radiated through the crown represents a large percentage of the total heat from the coal burned in a kiln, so that by using insulating bricks in the crown much of the loss can be prevented. It must be remembered that the hotter the outside surface of the crown becomes, the more heat will be radiated from it, and since radiation varies as the fourth power of the difference in temperature, a small reduction in the temperature of the crown will bring about a marked difference in the amount of heat radiated from it. (*b*) The foundations must be good, as, if the kiln " draws damp " from the foundation, the fuel consumption will be increased. (*c*) The kiln must be protected from the weather—preferably by the use of a roof of ample size quite independent of the kiln. (*d*) The heat which is not utilised in one part of the kiln must be utilised in another part of the same kiln (as in continuous kilns) or in another kiln (as in connected kilns); failure in this respect is the chief cause of high fuel consumption in single intermittent kilns. Some idea of the relative fuel consumption in burning firebricks to a temperature sufficient to bend Cone 7[1] in kilns of good design which have

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[1] For higher temperatures the fuel consumption rises very rapidly, and at Cone 14 it is frequently 35 cwt. per 1000 bricks, or 50 per cent. of the weight of the bricks.

been well built with consideration for fuel consumption, may be gained from the following figures, each of which is the average of those obtained from several works :—

(*a*) Up-draught oven	20 to 27 cwt.	per 1000 bricks.
(*b*) Down-draught kiln . . .	16 „ 18 cwt.	„ „
(*c*) Newcastle kiln	17 „ 19 cwt.	„ „
(*d*) Continuous kiln	7 „ 9 cwt.	„ „
(*e*) Connected down-draught kilns—		
No. 1 kiln, 16 to 18 cwt. No. 2 kiln, about 10 cwt. No. 3 kiln, about 9 cwt. } average	12 cwt.	„ „
(*f*) Single down-draught kiln (gas-fired)	14 to 16 cwt.	„ „
(*g*) Continuous kiln (gas-fired) . .	7 „ 9 cwt.	„ „
(*h*) Tunnel kiln	about 6 cwt.	„ „

Unless all these points are considered, an entirely erroneous idea as to the relative value of various kilns may be obtained. The most suitable means of comparison is to calculate the total amount spent on these items, together with 5 per cent. interest per annum on the capital and an allowance of 8 per cent. per annum for depreciation for a period of ten years. Compared in this manner, the much greater cost of erection of a gas-fired kiln is seen to counterbalance or even outweigh any saving effected by its use, except when temperatures above 1200° C. are to be attained.

Kiln Building.—It is not usually wise for the owner of a firebrick works to undertake the building of a kiln, but it is desirable that he should see that the most important parts of the kiln are properly constructed, and especially that the arches are well built, and that "filling" is not used instead of solid brickwork. It is equally important that ordinary bricklayers should not be allowed to build a kiln; even if it results in a saving at first, it is later the cause of much trouble and a heavy loss in damaged goods. The bond used in the best kilns is not the same as in ordinary bricklaying, but should be stronger, and most of the lining bricks should be laid as "headers." As little mortar as possible should be used, the great majority of the bricks being laid in fireclay slip (see Chapter XVII.).

Kilns should be sufficiently strong to render bracing and metal supports and ties unnecessary, and merely of a precautionary character. For rectangular kilns, the best bracing consists of steel rails, weighing at least 40 pounds per linear yard, placed vertically against the sides and ends of the kiln, with their lower ends embedded in the ground to a depth of 3 feet or more. The upper ends of the rails on the opposite sides of the kiln are then connected by a rod of steel about 1 inch in diameter, the ends of which are passed through the holes in the rails and secured by bolts.

The *maintenance of kilns* in a proper condition is very important, and this duty should be very carefully and skilfully carried out or serious losses may occur. The principal repairs required in kilns are in connection with cracks in the masonry (which may be due to various causes, including the sinking of the foundation and the repeated heating and cooling of the kiln walls), displacement of the arches, due to the same cause, and the replacement of bricks which have crumbled away. It is also important to have the kiln periodically examined and any cracks promptly filled up, or serious waste of heat will occur. The crown or arch of the kiln should also be frequently examined and kept in good condition, as a sagging crown not only fails to reflect the heat properly among the goods, but it is also a source of danger to men working inside or on the top of the kiln. The iron bars and bands used as ties should be examined periodically and tightened a little when necessary, as they tend to work slack on repeated heating or cooling. The space around the kilns should be kept quite dry, and the drains in good working order.

Burning.[1]—On burning, a fireclay is converted from a relatively soft and friable mass, which is easily disintegrated by water, into a strong, hard, stone-like material, which is highly resistant to water, acid, and most other solutions. These changes are brought about by the decomposition of the clay with evolution of water and, later, the formation of a partially fused mass which, on cooling, binds the other particles together.

The firing or burning of firebricks is similar in many respects to that of building bricks, except that much higher temperatures have to be reached with firebricks, and the risk of damage by overheating is much less serious.

Burning may conveniently be divided into five stages—

Stage 1.—Steaming or smoking.
Stage 2.—Decomposition of the clay and the removal of combustible and volatile matter.
Stage 3.—Full fire, the chief object of which is to so heat the goods that they will not shrink in use.
Stage 4.—Incipient vitrification.
Stage 5.—Annealing and cooling.

The *smoking stage* of firing is so called because a very smouldering fire is used in the kilns, the goods being heated by the "smoke." During this period any water of formation which has not been previously removed in the drying is driven off. This water forms a vapour or steam, and this "water-smoke" is sometimes stated to have given its name to this stage in the burning. Owing to the emission of steam, this stage of the firing is also known as *steaming*, and, during it, the object of the burner is to remove the water as rapidly and completely as possible without damaging the goods. Whilst some articles may be heated more rapidly than others, it is seldom safe to allow less than forty-eight hours for raising the temperature of any kiln (other than the small ones used for enamelling or testing) to 120° C. This is due to the weakness of the bond uniting the particles together; if the goods are heated too rapidly, the bonds will not be sufficiently strong to resist the strains due to the irregular expansion and contraction of the particles forming the goods. It may seem a serious waste of time to take so long to heat the goods to a temperature of boiling water, but experience has shown that under ordinary conditions of burning it is unavoidable.

The ordinary fireman never seems to realise how much water there is in the goods in the kiln; 300 lbs. per ton of goods is by no means an uncommon quantity, and as each pound of water forms, roughly, 27 cubic feet of steam, this means that over 8100 cubic feet of steam must be driven out of each ton of goods before the proper firing can be commenced; hence, the necessity for ample ventilation inside the kilns, and for sufficient time being allowed to effect the evaporation of the water without causing it to boil and so spoil the surface of the goods. It is on this account that a "smoky" fire is used at the commencement of the firing.

It is not always easy to tell how long to keep on the "smoking," the usual English practice of putting a cold bar of iron into the kiln and noticing whether any moisture condenses on it being a very rough, and by no means satisfactory,

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[1] The reactions which occur on heating clays are described in greater detail in the author's *Chemistry and Physics of Clays and Other Ceramic Materials* (Benn).

test. When it can be managed, the temperature should be measured by means of a thermometer; it should increase steadily from the start, and the "smoking" should not be stopped before all the goods have reached a temperature of at least 120° C. (or 250° F.).

The first stage may be regarded as complete when a self-registering maximum thermometer, inserted into any part of a kiln chamber containing goods, indicates a temperature of at least 120° C. The thermometer should be enclosed in a brass or copper tube, with a little asbestos packing, and about 4 yards of light chain should be attached to a ring at its upper end, in order that it may be lowered through the holes in the roof of the kiln to any desired depth. As the thermometer and chain are uncomfortable to handle when heated, a pair of padded leather gloves should be worn.

At the end of the first stage, the clay has merely dried as completely as possible. If the goods have not been overheated, and they were to be ground up with water, they would re-form into a pasty material almost identical with that from which they were first made. Hence, although its plasticity appears to have been destroyed, the clay is still potentially as plastic as before, and only requires the necessary amount of water to render it obviously plastic.

If the smoking is imperfectly carried out, the goods are apt to "fly," or unpleasant condensation products are formed on them. If the steam from the goods in the hotter part of the kiln were to condense as pure water, no further damage would result than that caused by the softening of the goods; unfortunately, the water thus condensed on the goods is never pure, but is often of a strongly acid nature, chiefly owing to the sulphuric acid produced by the oxidation of the sulphur in the coal. (A test has shown that this condensed water may contain about 30 grains of sulphuric acid per gallon.) Alkaline sulphates, hydrochloric acid, and ammonium chloride are also frequently present, and tend to cause discoloration or scum.

As the air passing through the kiln during smoking is the agent which really carries off the steam and other volatile matters, it is necessary to allow it sufficient passage; the damper the goods the more air will be required.

The *decomposition stage* follows immediately after the smoking; in many cases the two stages overlap slightly. In this second stage, the fires are caused to burn with moderate brightness, but the rise of temperature must be kept quite steady and slow. As the temperature increases to about 450° C. the expulsion of the "chemically combined water" begins,[1] and continues until a bright red heat is reached at about 700° C.

Clays differ greatly in the rate at which they lose this "combined water," and some do not become completely anhydrous until they have been heated to 1030° C., unless the heating is of extremely long duration.

It is a fact, which few clayworkers appreciate, that no matter how much a sample of clay may be dried, it still acts as though it retains a considerable amount of water. In a relatively pure clay, such as ball clay or china clay, about 13 per cent. of water appears to remain,[2] but ordinary fireclays may contain only about half this amount, and sandy marls and loams may contain even less, though some minerals occurring in commercial clays increase the

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[1] This is the generally accepted view, but it is probably more correct to state that at the temperature mentioned, the rate at which the combined water is evolved is much greater than at a lower temperature.

[2] It must be remembered that the existence of water, *as such*, in dried clay has not been proved. All that can be said is that on further heating the clay molecule is decomposed and water is one of the products formed. Recent investigations have indicated that clay is not a "hydrated silicate," but an alumino-silicic acid, the oxygen and hydrogen in it being combined as an essential part of the clay molecule and not existing as water.

proportion of this combined water. All clays contain an amount of combined water roughly proportional to the true clay and other alumino-silicic acids present, which cannot be removed without heating the clay to redness. Clays which have once lost their combined water can never be made plastic again, as the clay molecule has been decomposed and cannot be re-formed. They may absorb water in their pores, but they never combine with it.

During the removal of this combined water other changes occur. Any pyrite or marcasite present decomposes, losing a portion of its sulphur ; some carbon dioxide is evolved from the carbonates present, and the carbonaceous matter in the clay commences to burn. If the clay is removed from the kiln at the end of this period it is usually dirty grey in colour, very tender, and its form may be destroyed by rubbing with a piece of sandstone. The clay has lost its power of becoming plastic on treatment with water, but it has not yet become sufficiently hard and strong to be durable. These desirable characteristics will be gained in the " full fire."

Pyrite and marcasite usually decompose, and the ferrous oxide produced combines with silica to form fayalite, a very fusible silicate, which forms black spots in the bricks. If sufficient care is taken to raise the temperature very slowly and to provide an ample supply of air, the ferrous oxide can be oxidised to ferric oxide without forming fayalite, but on a commercial scale this is almost impossible.

In burning fireclays, there is seldom any trouble with the second stage of firing, provided it takes place slowly, if the temperature rises as steadily as possible. The goods are tender, yet, if the evolution of water is not sufficiently rapid to do harm, the whole of the second stage is often passed so easily that it is seldom noticed as a separate stage in the burning.

The heating of the kiln or oven may be more rapid than in the first stage, it being seldom necessary to take more than forty-eight hours for the second stage. Some burners complete it in seven or eight hours with goods of open texture.

According to Mellor, Le Chatelier, and others, clay goods at the end of the second stage of burning are composed of a mixture of free silica and free alumina, produced by the decomposition of the clay, together with free silica in the form of quartz, and any unaltered minerals which may have been present in the clay. It is possible, however, that the decomposition is not so simple as this, and that highly complex compounds are formed whose nature is by no means well understood. In either case, the clay has been decomposed and converted into a material which cannot be made plastic by any known method of treatment with water. It has shrunk slightly, become more porous, and has changed its colour to a small extent, though at this stage there are no signs of the final colour of the goods.

During the second stage, several complex changes occur in the minerals admixed with the clay ; thus, quartz and flint undergo a partial conversion into tridymite or cristobalite. Some of the most fusible impurities may commence to melt during this stage, and thus start changes which are more conveniently considered later, as occurring chiefly in the next stage.

To some extent the second and third stages overlap, and should be considered together.

The *full-fire stage* commences when the contents of the kiln have attained a temperature of about 900° C. The fires are then cleaned out and so fed and poked as to raise the temperature gradually, yet with moderate rapidity, first to a bright red heat, and later to the finishing temperature of the goods. The latter will depend on the purposes for which the goods are to be used ; it should never be below 1180° C. (Cone 5*a*), and for the better-class firebricks it will reach 1280° C. (Cone 9), 1350° C. (Cone 12), or even 1410° C. (Cone 14). The following are the most important changes which occur in the properties of the clay:—

(1) *Volatilisation* of carbon dioxide from the carbonates in the clay, of any volatile sulphur in the pyrite, marcasite, and other sulphides not driven off in the previous stage, and of any volatile carbonaceous matter, such as shale oil, which can be distilled completely or destructively in this range of temperature, occurs steadily throughout this stage of firing. The decomposition of the carbonates stretches over most of this period, and as soon as they have been decomposed, reactions between the bases (alkalies, magnesia, and lime) and the clay begin, forming the corresponding silicates, and probably some alumino-silicates. These do not fuse immediately; but in the fourth stage of firing, they effect the final fluxing.

A considerable portion of carbonaceous matter is burned out during this stage; gypsum and other sulphates are partially dissociated at a temperature of about 800° C., but so long as carbon is in the material the expulsion of this sulphur is hindered.

If the heating of the kiln is not too rapid, the volatilisation which occurs proceeds smoothly and causes no trouble.

(2) *Oxidation* of (*a*) ferrous carbonate, oxide, and sulphide into ferric compounds which, owing to the high temperature, usually produce black iron oxide[1] if the conditions are favourable for complete oxidation; (*b*) carbon to carbon dioxide, and of its compounds to carbon dioxide and water. The carbonaceous matter present, being both natural to the clay and purposely added in a variety of forms, may burn easily and steadily at a relatively low temperature; or, if of a coaly nature, it may produce a sudden rise in the temperature of the kiln, and may cause reduction and so prove very troublesome. Carbonaceous materials, such as coal, sawdust, and graphite, are often mixed with the clay. Thus, sawdust is added to form a porous ware, as it burns out and leaves corresponding hollows or pores. Ground graphite and coke are mixed with clay to be used in the production of crucibles, as they cause a more rapid heating of the metal and enable the mixture of carbon and clay to withstand high temperatures and sudden changes better than clay alone.

If the temperature rises rapidly without the oxidation of the iron and the carbon in the clay being complete, various discolorations will be produced and slag spots will be formed, and may even cause the clay to lose its shape at too low a temperature. This is particularly the case with shale containing bituminous matter, as the kind of carbonaceous matter present necessitates the careful regulation of the temperature of oxidation. If the clay contains bituminous carbon, oxidation must proceed at a far lower temperature than when the carbon is similar to that in anthracite, as there is the distillation as well as the burning of the hydrocarbons to consider. The higher the temperature, the more rapidly these hydrocarbons will be evolved, and they may produce a pressure which swells or bursts the ware. In any case, if the heating is too rapid, the gas produced will flash into flame and raise the temperature very rapidly, so that it may reach the vitrification or even the softening point of the clay, and so spoil the goods.

Care in the first two stages, and especially when the goods are at a dull red heat, together with sufficient time to permit all the carbonaceous matter to burn away and the iron compounds to become fully oxidised, are the two

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[1] Red ferric oxide (Fe_2O_3) is first produced, but is decomposed when the temperature is sufficiently high, forming black magnetic oxide (Fe_3O_4).

essentials for success at this portion of the burning. The end of the oxidation period must be ascertained separately for each clay by withdrawing samples at intervals and breaking them open. If they contain black cores of carbonaceous matter the oxidation is incomplete, and the heating must be continued with an ample supply of air until a sample withdrawn from the kiln shows no dark centre on breaking (see *Hearts*, p. 322).

Failure to complete the oxidation of the carbon present means that, as soon as the temperature is high enough, the iron will combine with the silica to form ferrous silicate, which vitrifies or fuses suddenly, thus enclosing that portion of the brick still containing carbon. Any carbon dioxide or monoxide forming will cause a pressure which bloats the bricks or at least causes the structure of the clay to become vesicular and weak at a temperature far below the proper vitrification temperature, where the iron is present as ferric oxide. Information on the effect of oxidation on the *colour* and *porosity* of clay should be sought under these headings.

(3) *Reduction* of sulphates to sulphides and the production of slag-like silicates of iron may easily occur with certain clays if they are heated with an insufficient supply of air. Pyrites is particularly troublesome in this respect, as it requires exceptionally careful treatment to secure its oxidation, which is seldom complete in clays containing this substance.

The ferric sulphide is dissociated, forming ferrous sulphide, and this, in the presence of carbon and some air, forms ferrous oxide. This at once combines with the silica in the clay, if the temperature is sufficiently high, and forms a dark slag.

Sulphates are reduced to sulphides by carbon, and they then undergo the same reactions as pyrite and other sulphides occurring naturally in the clay.

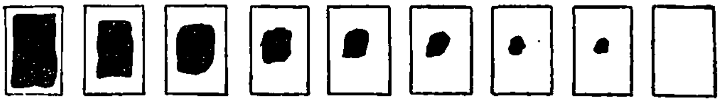


FIG. 77.—Showing progressive diminution of a dark core on prolonged heating in air.

In this connection, the effect of pyrite in the coal used in heating the clay must not be overlooked. The sulphur dioxide so produced is a powerful reducing agent, and may cause discoloration by its action on the iron oxide in the clay. Sulphur trioxide produced at the same time from the burning fuel may attack the bases in the clay, producing sulphates, which may form scum under exclusively oxidising conditions, but which will be destroyed if the conditions are alternately oxidising and reducing.

Carbon cannot be fully burned except in the presence of air in direct contact with its particles, so that if the air supply is deficient, or if for any reason it cannot get to the carbon—as when a clay is dense—the effects of reduction will be observed. As carbon prevents the liberation and expulsion of sulphur from clay, it may be the indirect means of causing the latter to swell, as described under *Oxidation*.

Another cause of swelling is as follows:—As the temperature rises and vitrification proceeds, bubbles of gas—chiefly oxygen—are produced. These bubbles are contained in so viscous a material that they cannot escape from it at all readily; they, therefore, remain in the material as sealed pores, and cause a corresponding reduction in the total or true porosity of the material. When the formation of bubbles is very rapid and extensive, some gases escape to the surface of the goods and leave characteristic blisters or blebs.

This swelling of the material is much greater in some cases than in others, but it occurs in all fireclays which are heated for a long time at a temperature at which vitrification occurs with fair rapidity; with many fireclays this is at the melting-point of steel (about 1500° C.).

Hearts—dark coloured or *black cores*—in bricks (fig. 77) are usually the result of reducing conditions in their interior, the pores nearer the surface becoming closed and so preventing access of air to the centre of the bricks. This defect is sometimes attributed to placing the goods in too damp a condition in the kiln, but the only difference made by the presence of the water would be to increase the time needed during the first stage of firing. If no such extension of time is allowed, the effect will be the same as a sudden rise in temperature; the pores will close and, by preventing all the carbonaceous matter being oxidised, will produce the effect of a reduction. These cores may be prevented by avoiding reducing conditions (see *Oxidation*). If the clay be alternately heated in an oxidising and a reducing atmosphere, a change of colour, increasing with the number of alternations, is produced.

Too rapid heating of the kiln at a temperature below 900° C. is the cause of much clay being spoiled, because the carbonaceous matter it contains is decomposed and " set " in such a way that it cannot afterwards be burned out without spoiling the colour of the goods. By heating slowly with plenty of air and drawing trials occasionally the gradual reduction of the cores may be observed, as in fig. 77, which represents a series of successive bricks drawn out of the kiln and broken across their centres.

In works where the clay shows a strong tendency to form cores or " hearts " and the burning is, in consequence, particularly difficult, it is often advantageous to mix a considerable amount of burned fireclay (grog) or even sand with that used for brickmaking, in order to produce a more porous material, and one in which the pores cannot so readily be sealed during the burning. A similar result, without the same risk of producing a weak body, follows from using a more coarsely ground clay or by making the bricks, etc., by the semi-dry process instead of from a plastic paste.

All these modifications are intended to increase the porosity of the material and so enable a freer circulation of air within its pores. Any means which will secure ample circulation without causing a premature closing of the pores will effectively prevent the formation of cores or " hearts."

Owing to the greater difficulty experienced in regulating the amount of air passing through them, Hoffmann and tunnel kilns are less satisfactory with core-producing clays than are intermittent or continuous chamber kilns.

(4) *Porosity*, which is due to the spaces between the particles of clay, increases gradually during the first stage of firing, and reaches a maximum when all the carbonaceous matter has been removed, but before vitrification has commenced. In some clays with numerous yet minute pores, the carbon is never completely expelled, and the porosity of such clays reaches a maximum soon after the commencement of the second stage of firing, at a temperature of about 750° C. to 850° C.

If the water and carbonaceous matter have been removed from between the particles in the manner already described, a certain amount of pore-space is left (notwithstanding the shrinkage of the clay), and it is this which gives the fired material its porosity or power of *absorption* at this stage. The porosity will, therefore, depend on the extent to which the clay particles fit into each other and the amount of carbonaceous matter present in the unfired or " green " clay.

As a rule, the purer the clay and the finer it is ground, the less will be its porosity. Overheating the clay will diminish its porosity by causing a partial vitrification of the material, the resultant glassy material filling up some of the interstices formerly occupied by air.

When other materials are mixed with the clay, with a view to lessening the contraction, the porosity is also affected according to the nature and proportion of the added ingredients. If these are composed of carbonaceous matter, such as sawdust or coal, the porosity of the fired clay will be much higher than if sand or other non-combustible material had been used. If, on the contrary, the clay had been mixed with a low-melting clay, felspar, Cornish stone, or some other flux, the porosity would be diminished owing to vitrification. As the porosity of the clay gradually diminishes with prolonged heating, its measurement forms one of the most convenient means of determining the point at which the heating should cease in the manufacture of goods from clay.

At the point of maximum porosity, a piece of heated clay is usually near its maximum strength; as the porosity diminishes owing to increased vitrification, the strength of the hot material decreases until a point is reached when, on further heating, a sufficient portion of the mass has become fluid for the clay to lose its shape. This is, however, only true of the intensely hot material. As soon as it is allowed to cool, the fused portion solidifies to a hard glass which binds the remaining particles of material together and forms an intensely strong mass. The clayworker is, therefore, in a dilemma; if he heats his material sufficiently to produce a considerable amount of vitrification, he runs the risk of the ware collapsing in the kiln, whereas, if he heats it less strongly, the ware will not, when cold, be as strong as similar ware which has been more vitrified.

The end of the third or " full fire " stage may, therefore, be defined as being the point at which the porosity of the clay begins to diminish somewhat rapidly owing to incipient vitrification.

(5) *Colour changes* occurring during the heating of the clay are most noticeable in the third stage of firing. If the raw clay contained organic matter this will have been partially or completely burned away, leaving the material black or grey with the charred carbon, or white, buff, red, brown, or " blue " according to the "impurities" present and the method of heating. Hence, the colour shown by clay after burning depends upon its composition and the character of the firing conditions. Thus—

(i) Clays fairly high in alumina and with a moderate iron oxide content (about 3 per cent. of the latter) are buff-burning.

(ii) Clays high in alumina and low in iron burn white or light buff.

There is little or no connection between the colour of a raw clay and that after firing, and the effect of heat on colour can seldom be predicted with certainty.

Most iron compounds in clays produce a red colour (as in red building bricks), except particles of iron sulphide (pyrite), which do not give a wholly red colour to the clay, but invariably show up as black or slagged spots (sometimes accompanied by a little red colour where the iron has been fully oxidised to red ferric oxide), owing to the combination of the ferrous oxide with silica, immediately the iron has parted with its sulphur. Some black spots in well-burned firebricks may be composed of magnetic oxide.

Reducing agents, such as carbon and sulphur compounds, do not of themselves affect the colour produced by the iron, but they prevent or delay the iron from playing its customary rôle, and consequently, may cause untold trouble in the burning, especially with pyritic and bituminous fireclays, as already described.

The oxidation or reduction occurring during the heating of clays containing iron compounds has a far greater effect on the colour than the proportion of iron present, and an error made in the early stages of the firing can seldom be fully repaired later. Thus, if the iron oxide has been reduced by the carbon in the clay, and has afterwards been apparently fully oxidised, it never assumes its true colour. The change in colour produced by exposing the clay alternately to an oxidising and reducing atmosphere is known as *flashing*. The colour produced depends on the number of alternations and on the intensity of oxidation or reduction. It is often characterised in fireclays by a reddish-brown colour (oxidised, or ferr*ic* compounds) accompanied by black spots (reduced, or ferr*ous* compounds).

In clays which are burned at a temperature exceeding 1200° C., it is practically impossible to admit any excess of air, and some amount of reduction almost always occurs at this temperature.

At the conclusion of the third stage, if this part of the burning has been properly managed, all the carbonaceous matter present should have been burned out by conversion into harmless gases; most, if not all, the salts present as impurities should have been decomposed into the equivalent oxides or silicates the decomposition of the clay should be complete, and the inversion of any quartzose material should have made good progress. In some cases, the colour and several properties will approach to, or may be the same as, that of the finished goods.

The result of heating pure clay to the completion of the third stage is to produce a white, porous mass of moderate mechanical strength. The composition of the material is not certainly known, some authorities regarding it as a mere mixture of silica and alumina, whilst others maintain that it is a compound (anhydride) of aluminium and silicon. Most clays contain sufficient impurities to produce a certain amount of vitrified matter, and introduce questions which are best considered in the fourth, or finishing, stage of the burning.

It is often convenient to distinguish goods which finish burning at the third stage from those which have passed through the fourth stage by designating the former as *baked* and the latter as *burned*. The distinction is by no means sharp, but it is convenient, and is much used. Care should be taken not to apply it too stringently; thus, gas-retorts should be burned at a much higher temperature than some stoneware, yet they are porous (whilst stoneware is quite impervious), and may be regarded as "baked." Moreover, even in so-called "baked" goods, a certain amount of vitrification is necessary in order to bind the particles together.

The stage of *incipient vitrification*, or fourth period of firing, is said to commence as soon as the amount of fused material produced is sufficient for its presence to be detected.

At the commencement of the fourth stage of burning, the goods are in the form of a porous mass of amorphous material, but as the heating progresses the vitrifiable matter melts, flows among the pores, and gradually fills some of them with a sort of glass. On further heating, this glassy material attacks and dissolves some of the unmolten material and becomes more viscid. In this way, the nature of the goods is gradually changed from a porous and unfused mass to a similar mass in which the pores are partly filled with glass, and eventually (if the heating were to be excessive) the proportion of molten material would be so large that the "skeleton" could not resist its softening action, and the goods would become misshapen or might even form a shapeless mass.

In consequence of the impurities they contain, ordinary clays do not melt at sharply defined temperatures; on the contrary, the most fusible constituents melt first, and the others follow later; a considerable amount of reaction also occurs between the different materials, and may result in the formation of new compounds which are more refractory than any of those originally present. In the case of fireclays the crystals of mullite ($3Al_2O_3.2SiO_2$) formed by these changes produce a felted mass of highly refractory crystals, which forms the greater part of the skeleton in firebricks of the best quality. In inferior firebricks little or no mullite may be present, because the conditions of firing have not been favourable to its formation.

The production of mullite occurs automatically at temperatures exceeding 1250° C., the rate of formation increasing rapidly as the temperature rises, though conversion is seldom if ever complete even at 1500° C. Heat alone is not sufficient; there must be enough impurities in the clay to form a molten glass which slowly attacks the hot firebrick material and dissolves it, and from which mullite crystals then separate out. The dissolution followed by the separation of mullite crystals continues so long as the requisite temperature is maintained and there is material present from which the mullite can be produced.

Too large a proportion of vitrified (glassy) material is objectionable, because it (i) increases spalling by making the bricks too rigid at low and moderate temperatures, (ii) reduces the strength of the hot brick, and (iii) increases the amount of corrosion by being itself a corrosive agent at high temperatures.

The stage of incipient vitrification (or of reduction of porosity) is the *finishing-point* of the burning of firebricks, but at the temperature at which most fireclays are burned the amount of fused material is so small that it is difficult to recognise it without special methods, such as the determination of the porosity of the material at various temperatures, some of which are below and others above that at which incipient vitrification occurs. In actual work, the manufacturer uses other methods to determine when the heating of the kiln shall be stopped. These are often crude and unreliable.

The *finishing temperature* should depend on the clay used, but, in practice, other matters—such as the selling price of the bricks—are taken into consideration, with the result that the different firms vary greatly in what they consider to be the most desirable finishing-point for their purpose. This is unsatisfactory to the user of refractory goods, for one firm will supply him with bricks burned at, say, 1200° C., whilst another will offer bricks burned at 1500° C., the latter being much better in every way, but more costly on account of the higher finishing temperature. Much injustice would be avoided if firms were to guarantee that their goods were burned at a certain temperature, or that they would not shrink if burned for a certain time at a temperature to be agreed upon.

Fireclay bricks are "finished" at various temperatures in different parts of the country, that corresponding to Seger Cone 5*a* being quite common. Much better bricks are obtained by finishing at Seger Cone 7 to 12, and still better ones at Cone 14 or above.

A wise rule well worth general adoption is to fire the goods to a higher temperature than they will ever meet in actual service, whilst in Great Britain any temperature which will give the bricks a saleable hardness and "ring" is considered sufficient by most makers, though a few British manufacturers have the sense to use a higher finishing temperature.

The object of the higher finishing-point is to prevent any further action taking place in the bricks when they are in actual use, and it is found that for this reason, amongst others, many Continental fireclay goods are more durable than those made in this country. It is not always necessary to burn firebricks to the temperature at which they are to be used, as only a small proportion of each brick attains the temperature of the furnace. The exposed surface of the bricks may, however, be heated to a temperature which is well above that which the bricks are required to withstand when in use; such re-heating should be prolonged to enable a sufficiently thick "skin" of resistant material to be formed (see also *Re-burning*).

Whilst the prices obtained for most of the fireclay bricks in this country will not admit of their being fired at the higher temperatures mentioned, there is no question that for the exacting requirements of metallurgists and gas engineers the harder-fired bricks are the only ones likely to prove satisfactory, and prices must be arranged accordingly.

The amount of vitrification necessary depends largely on the class of ware to be made. Firebricks require very little vitrification, whilst refractory porcelain is vitrified almost completely.

Owing to the refractoriness of firebricks, it is not usually possible to ascertain by any simple test whether they have been sufficiently burned. It is, therefore, customary to continue the heating until they have shrunk to a pre-determined extent, or to use Seger cones to indicate the temperature reached in the kiln.

To ensure adequate burning, many users of fireclay bricks now require that such bricks shall conform to a specification such as that issued by the Institution of Gas Engineers (p. 810), in which a "reheating" or "after-contraction" test is included. This test is quite suitable for bricks required in gas-works, but for some other purposes a higher re-heating temperature should be specified.

The duration of the heating at or near the finishing-point has a great effect on the goods. This prolonged heating at a constant temperature is known as *soaking*, and it is very essential in order that the contents of the kiln may be heated uniformly, as heat penetrates them very slowly. The time required for such "soaking" depends on the individual material and on the finishing temperature, and so must be ascertained by actual trial.

The heating of the kiln to a dull red heat usually occupies forty-eight hours; a further period of forty-eight hours is required for the contents to attain a temperature corresponding to Cone 5*a*; the full time needed to finish the heating naturally varies with the maximum temperature to be attained and the length of time the bricks are to be kept at or near this temperature.

Precautions.—The most important precautions required to be taken in the burning of firebricks are—

(i) *An ample supply of pure air*, as and when required. The control of the air supply is sometimes regarded as a matter of difficulty, and, in spite of its importance, few burners pay sufficient attention to it. Yet they are all aware of the fact that an insufficient supply and an unnecessary excess of air are equally harmful, the former in damaging the goods and the latter in causing serious wastage of fuel. In most cases, the control is comparatively easy to an intelligent man. In order that the air may be used efficiently, it should be hot. This creates a difficulty in the case of single kilns, and is one reason why continuous kilns are more economical.

(ii) *A regular supply of fuel* and a proper cleaning of the fires, so that the temperature may rise steadily. The burner must feed and care for the fires with skill and intelligence, as well as with diligence. This regularity of adding coal is exceedingly important, but the difficulty is to be sure that the burner is as regular as he is supposed to be. Even if he is given a good watch or clock, it does not follow that he always looks at it. In the night-time especially it is difficult for him not to miss an occasional " quarter," or even two or three together, and serious and " unexplainable " results may then occur in the firing. This may be avoided in a very simple manner by the use of a recording draught gauge (fig. 76).

(iii) *Steadiness in heating* is very important. It is usually better to heat too slowly than too rapidly, though the former may result in an unnecessary waste of fuel. The great drawbacks to slow burning are reduced output, the extra cost of the fuel, and the need for added care and watchfulness on the part of the burner.

Cambridge & Paul Instrument Co., Ltd.

FIG. 78.—Féry radiation pyrometer.

When burning slowly, special precautions must be taken or the amount of fuel used will be excessive. The spaces between the goods should be larger, the trace holes, or flues, near the base of the kiln should be wider, and the kiln filled nearer the top than when burning more rapidly, as with slow burning a more feeble draught is needed, and there is great risk of this being drawn over the top of the goods instead of uniformly through them. The slower the heating, the greater is the necessity for skilful setting, as there is a liability of the burner being held back in his work by the irregular progress of the fire if the setting is too close or is irregular. Such a delay may ruin the goods.

There are few burners who are not dependent on the weather, because this has a great influence on the draught, particularly in summer. It is frequently observed that the kiln makes but little progress during the day, but it is easy to work at a normal rate during the night. In some weather, the variations of the draught are so sudden and frequent that it is impossible to control the burning when a chimney is used, and all that the burner can do is to feed so lightly that no harm will result until the storm has passed; afterwards he can work as usual, though it is quite impossible to avoid the loss of time which has been incurred. These variations in draught can be avoided entirely by the use of a satisfactory fan; but there are few brick manufacturers who have yet realised the value of a fan in place of a chimney. The reason is that most brickyards already have chimneys, and a man starting a new works will be more inclined to use a chimney about which he thinks he knows something rather than instal a fan about which he knows less.

If clay goods are heated too rapidly they are almost invariably spoiled, distortion cracks and discoloration being the chief defects which result from this treatment. No general rules can be given as to the time required, as so much depends on the goods and the type of kiln used. This matter will, therefore, be considered later when dealing with the various kinds of goods.

In order to secure an effective control of the heating and to determine whether the time has arrived for finishing the burning, some form of indicator is necessary.

The principal instruments employed for this purpose may be divided into four classes—

(*a*) Temperature measurers, including thermometers and pyrometers. These are well known, especially on the Continent and in the United States.

(*b*) Heat-effect indicators or pyroscopes, such as Seger cones, Holdcroft thermoscopes, and other arrangements in which the change in shape of a piece of selected material is observed. These are also well known.

(*c*) Gauges used to measure the amount of shrinkage or expansion of the ware.

(*d*) " Trials " based on other properties.

Besides these are recording draught gauges and combustion recorders, *i.e.* apparatus for automatically making a long series of partial analyses of the flue-gases at short intervals.

Many skilled burners rely solely on their eyes in ascertaining the finishing temperature of a kiln; but to do this requires exceptional skill, as the " colour " of the contents of the kiln appears to be brighter at night than by day, and in winter than in summer. It is always preferable to use a pyrometer or pyroscope, or to measure the shrinkage of the goods, particularly when burning those of great importance.

Cambridge & Paul Instrument Co., Ltd.

FIG. 79.—Thread recorder for Féry pyrometer.

Thermometers are only available up to a temperature of about 360° C., and their use is practically limited to the first stage of burning. For this purpose, a self-registering maximum thermometer, encased in a brass tube and attached to a light chain, is the most convenient.

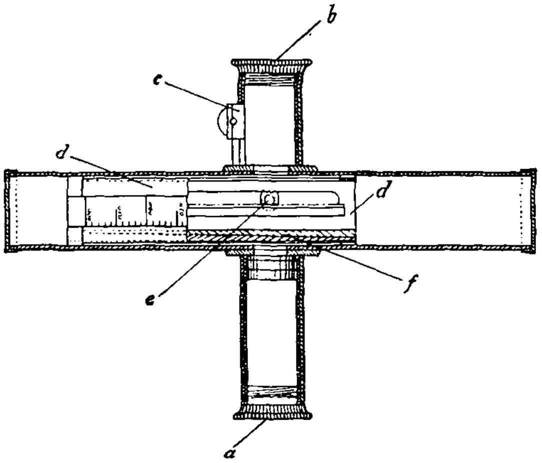
The *pyrometers* available for the high temperatures required for burning refractory materials are, in practice, limited to radiation pyrometers and optical pyrometers, as thermo-electric and electric-resistance pyrometers are not suitable for prolonged use at temperatures exceeding 1300° C., though they may be used occasionally and momentarily at higher temperatures.

Radiation pyrometers depend on the fact that the radiation from a " black body " is proportional to the fourth power of its temperature, so that by collecting the radiations from the interior of the kiln by means of a suitable mirror, and concentrating them on a small thermocouple attached to a suitable indicator, a record of the temperature of any part of the kiln may be obtained in a continuous curve without any appreciable wear and tear on the instrument itself. Such instruments are, therefore, very valuable for recording the temperatures attained in firebrick kilns, and may be used for any temperature above 400° C. Various types of radiation pyrometers are on the market, a very convenient one being the Féry mirror-pyrometer supplied by the Cambridge & Paul Instrument Co., Ltd., and shown in figs. 78 and 79. This pyrometer consists of a thermo-electric device into which the heat radiated from an object is concentrated by means of a mirror which is capable of being moved by a rack and pinion so as to focus the rays very accurately upon the thermo-junction. The whole is enclosed in a protective case, which renders the instrument very durable if care is taken in its use. This instrument should be used in conjunction with a suitable recorder, such as a " thread recorder," shown in fig. 79. A similar instrument with a fixed focus is supplied by the Foster Instrument Co.

Radiation pyrometers should be under the care of a suitable man, as it is very important that they should not be damaged, or difficulties will arise and incorrect readings may be obtained.

Optical pyrometers may also be employed for measuring high temperatures. Like radiation pyrometers, they are kept wholly outside the kiln, and the temperature is measured by the intensity of the luminous rays from the particular point in the kiln of which the temperature is desired. Various forms of optical pyrometers are now available, the principal forms being—

(i) Those in which the radiations from the kiln are compared with a coloured glass, which is calibrated so as to indicate the temperature by direct reading. The Lovibond and Wedge pyrometers are of this type. The Wedge pyrometer (shown in section in fig. 80) consists of a telescopic tube across which can be moved a wedge of dark glass so as to bring any thickness of glass into the tube. The observer looks at the interior of the furnace through the tube, and adjusts the position of the wedge until the light is just invisible, and reads the temperature on a scale on the instrument. The Wedge pyrometer is simple in construction and requires very little skill in handling, and is, therefore, very useful for approximate measurements, but it is not so accurate as some of the more elaborate instruments.



Optical Pyrometer Syndicate.

FIG. 80.—Wedge pyrometer.

(ii) Those in which the radiations are compared with a variable light, such as that from the filament of an electric lamp, the current supplied to the lamp being a measure of the temperature. This class includes the Holborn-Kurlbaum and Siemens pyrometers and the Leeds-Northrup pyrometer. In most of these instruments the images of the light and kiln appear side by side, but in the Leeds-Northrup pyrometer the electric filament is placed so that the kiln forms a background to it, and the resistance of the lamp is varied so as to alter the intensity of the filament until it is just invisible, the resistance then being a measure of the temperature of the kiln. The chief disadvantage with optical pyrometers of the types in this group is that the filament gradually deteriorates, and frequent standardisation is necessary in order to secure accurate results.

(iii) Those in which the radiations are compared with a standard flame, either directly or by the light thrown on a screen, as in the Le Chatelier and Wanner pyrometers. The Le Chatelier pyrometer is excellent for research work, but it is too delicate to be placed in the hands of a burner. Similarly, the Wanner pyrometer, in which the light from the kiln is compared with a standard amyl acetate lamp, requires considerable skill in handling, and is, therefore, seldom employed in clayworks. Frequent standardisation is necessary to ensure accurate results.

Before firing. After firing.

FIG. 81.—Holdcroft's thermoscopes.

From a lengthy experience of all the pyrometers mentioned, as well as several others, the author has found that the Féry or Foster pyrometer, with recorder, is the easiest to use and the most accurate so far as kilns for refractory materials are concerned.

Pyroscopes usually consist of a mixture of silicates moulded into a definite shape, which is altered when the pyroscopes have been subjected to a definite heat treatment. Such pyroscopes do not register temperature as such, but heat effect, though they are often quoted as if they indicated temperatures. The pyroscopes chiefly in use for firebrick kilns are—

(i) *Holdcroft's thermoscope* (fig. 81), which consists of a series of numbered bars supported at their ends; they sag at the middle when their indicating temperature or heat-treatment has been reached. By inserting three or four such bars into the kiln on a suitable holder, such as the one shown, warning is given of the nearness of the finishing-point by the sagging of the most fusible bars, and, by including one bar which melts at a higher temperature than the finishing-point required, it is easy to tell whether the goods have been over-fired.

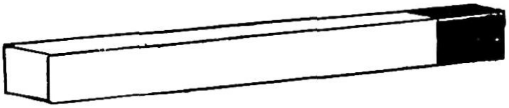


FIG. 82.—Calorite.

(ii) *Calorites* (fig. 82), which are supplied by Wenger's Ltd. of Etruria, Stoke-on-Trent, are very similar to thermoscopes. They are painted at one end to indicate the temperature at which they bend, and are suitable for temperatures from 500° C. to 1470° C.

(iii) *Seger cones* are small tetrahedral pyramids about 2½ inches high,[1] and

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[1] A series of smaller cones is supplied for experimental work and testing at the highest temperatures.

are composed of a suitable mixture of felspar, china clay, and quartz; those for medium temperatures also contain certain other fluxes, such as iron oxide, marble, and boric oxide. They are made to indicate a series of temperatures differing from each other by about 20° C. or 36° F. The cones are pressed sufficiently firmly into a small block of fireclay (or a mixture of china clay and alumina) to enable them to stand firmly, but in no case to a depth of more than ⅛ inch. They are then placed in a suitable position in the kiln, where they can be seen through a sight-hole in the wall. Several sets of cones should be placed in different parts of the kiln, especially if the temperature of the interior is not likely to be uniform in various parts of the chamber. It is usual to protect the cones from flame or falling dust by placing them between and under bricks or slabs. As the firing proceeds and the temperature rises sufficiently, each cone, in its turn, gradually bends over, the "indicating point" being when the tip of the cone touches the base of the support.

Seger cones do not always melt at the same temperature, but are influenced, as shown by R. Rieke, by the atmosphere and the rate of heating. If the heating is excessively prolonged, Cones 022 to 013*a* melt at a lower temperature than is anticipated, whilst Cones 012*a* to 1*a*, under the same conditions, develop a hard refractory skin, possibly due to the removal of volatile constituents, or the production of refractory silicates. The same phenomena were investigated by Bradshaw and Emery,[1] who found that, when Seger Cone 08*a*, and other, more refractory, cones are heated in a reducing atmosphere, the exterior becomes very hard, whilst the centre fuses and runs out, but the cone retains its shape and does not bend. The hardening is attributed to the formation of a thin film of hard refractory carbon on the surface of the cone.

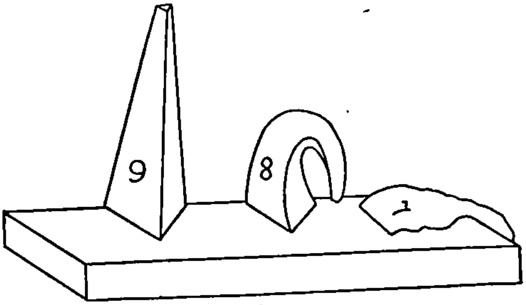

FIG. 83.—Seger cones.

Rieke also found that Cones 2*a* to 17 softened at a lower temperature on very prolonged heating, the difference being greatest with Cones 6 to 9, the bending points of which varied as much as 80° C. to 100° C. from the scheduled temperature.

As shown in fig. 83, the cone at the right-hand side of the illustration has been overheated; the centre cone has been heated exactly to the temperature it is intended to indicate, and the remaining cone has not begun to bend, thereby showing that the desired temperature has not been exceeded. It is always desirable to arrange the cones in groups of three consecutive numbers so that the first cone warns the burner that the kiln is approaching the finishing-point; the middle cone indicates the finishing-point; and a "guard cone" shows that the contents of the kiln have not been overheated.

In comparing pyrometers and pyroscopes, etc., it should be noted that a sensitive pyrometer will indicate the temperature much more rapidly than the goods themselves, and that if the kiln is considered to be "finished" as soon as the pyrometer (of whatever make) indicates a certain temperature, perfect goods

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[1] *Trans. Eng. Cer. Soc.*, 1921–1922, **21** (ii), 117.

will not be obtained. The temperature must be maintained for a sufficient time, particularly with some goods. When Seger cones are used, the length of this maturing time is so short as to be practically negligible, because the cones themselves take a certain time before they bend over completely. This slight disadvantage of the cones for certain purposes is an actual gain to the clayworker, as it saves him from worrying about the time to continue his heating; he may usually consider the kiln as finished as soon as the desired cone has bent over until its point just touches the clay on which the cone stands.

Shrinkage and expansion gauges exist in a variety of forms, from the small one devised by Josiah Wedgwood, or a very accurate micrometer gauge, to the comparatively crude use of a measuring rod inserted in the top of the kiln. For controlling the burning, this last is quite suitable, as it measures the shrinkage of the total height of the bricks in the kiln (usually about 8 feet), and on this account it gives a very accurate measurement of the shrinkage.

The usual method of measuring the shrinkage or " settlement " of fireclay bricks or the expansion of silica bricks[1] is based on the fact that, during the burning, the fireclay bricks in the kiln settle slowly down so that there is a fair space between the top of them and the kiln arch at the end of the firing, though at the beginning the kiln was full up to the top. The difference in the height of the goods may easily amount to 10 to 12 inches, or even more with some clays. It is measured by means of a gauge, which usually consists of a plain steel rod about 4 feet in length, graduated in inches, and fitted with a loosely sliding cross-piece held by a spring, so that it remains in the position in which it was last placed. The cross-piece is pushed down towards the zero of the bar, and the latter is then passed through a small opening in the top of the kiln until it reaches the top of the contents of the kiln. As the cross-piece cannot pass through the opening, it acts as an indicator of the distance between the top of the kiln (outside) and the goods inside. The position of the cross-piece on the bar is noted. At intervals during the burning, the bar is again inserted until its lower end touches the top of the goods being burned, and the position of the cross-piece is again noted. When the bricks have shrunk or expanded to the desired extent, the burning is regarded as finished. Thus, a gauge registered 22 inches before the burning commenced, and when it registered 30½ inches the goods were regarded as sufficiently burned, as they had shrunk 8½ inches. The actual numbers on the gauge are of no general importance; it is the amount of shrinkage, *i.e.* the difference between the first and last readings, which is important.

Each kiln has its own measurements, the goods in some of them needing to settle several inches more than in others, but the burner soon learns to know their differences; these are mostly due to the way in which the bricks are set and to the thickness of the kiln arch. Probably the settling shows better than any other simple test whether the goods have been fully burned.

It is not, however, safe to rely merely on the shrinkage or expansion of the goods to determine the finishing-point of the kiln, as clay has a great tendency to contract irregularly, or a slip in the goods may cause them to shrink unduly, but as a simple confirmation of other tests, this measurement is of considerable value and should never be omitted.

Wedgwood and others have devised gauges for measuring the change in the size of test-pieces removed from the kiln. Whilst excellent in many ways, it is generally considered that these are too delicate for use by burners.

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[1] This method obviously cannot be used for semi-silica bricks, which retain their volume during burning.

Trials of various kinds, consisting of bricks or blocks taken from the kiln at intervals and examined as to their colour and fracture, are largely used, and are of considerable value in careful and experienced hands. They are of more importance in glazed or vitrified ware than with firebricks, though they are unsurpassed as a means of controlling the earlier stages of burning some difficult clays (see fig. 77).

Time-temperature Charts.—No matter whether a recording pyrometer is used or not, it will be found desirable to prepare a time-temperature chart or schedule which will act as a standard for the firemen, and if the changes in the temperature of each kiln are marked on a series of such charts, a direct comparison can easily be made. A comparison of these diagrams with the ware from the kilns usually enables very considerable improvements to be made in the quality of the ware, the consumption of fuel, and the time spent in firing and cooling. Irregularities in firing are clearly shown and other minor advantages are obtained. A supply of standard charts for each kiln can be printed lithographically (in red) for a small sum, and they have proved invaluable in many cases in the author's experience. In order to keep the chart within reasonable limits of size, it is generally advisable to allow each $\frac{1}{25}$th of an inch to represent 10° C. or one hour respectively.

In a temperature diagram such as that shown in fig. 84, the vertical distances represent the temperature, and horizontal ones the time ; hence, a point on the diagram which is on both a temperature and a time line will indicate the temperature of the kiln at that particular time. Such a diagram will be automatically drawn by pyrometers fitted with an automatic recorder, but in other cases they may be made out by observation as follows :—

The time of lighting the kiln is noted, and at sufficiently frequent intervals the temperature of the kiln is ascertained by means of a thermometer, a pyrometer, or a pyroscope. The time of each observation is carefully noted on a chart in small squares, in which the horizontal lines represent degrees of temperature and the vertical lines represent hours after lighting the kiln by marking with a fine dot the meeting-place of each line corresponding to a certain observed temperature with the line corresponding to the time of the observation. The dots indicating the other observations are then joined together by a fine ink line, and so produce a curiously shaped line somewhat resembling the one illustrated, and known as a " time-temperature curve." As the temperature of the kiln increases, the curve will tend to rise towards the top of the chart until the highest temperature of the kiln is reached, after which it will gradually descend[1] until it reaches the level from which it started ; the kiln is then perfectly cold. The dotted line shown in the figure indicates the shape of the " curve " if the heating and cooling had been perfectly regular. It will, of course, be understood that this chart will only show serious variations in the temperature of the kiln, but in spite of this disadvantage, it is of great value in accounting for otherwise inexplicable variations in the quality of the goods.

Closing.—As soon as the finishing-point is reached, the various openings into the kiln are all closed and luted with fireclay paste. This closing distributes the heat uniformly in the kiln. It often produces a slight rise in temperature, accompanied by strong reducing conditions, known as the *jump* or *afterglow*, which are understood to make the bricks somewhat tougher than if the kiln were allowed to cool immediately the finishing temperature had been reached.

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[1] When a kiln is maintained for a length of time at the finishing temperature, the curve will be rounded or flattened instead of sharp as at E. It is usually desirable to finish the burning of firebricks at not less than 1280° C. (or 2336° F.), though the point indicated by E is a common finishing temperature.

This *jump* cannot be obtained so readily in continuous or tunnel kilns, as the latter do not admit of complete closure.

Firebricks can often be improved in colour if a number of small openings are made in the walls of the kiln about two hours after the completion of the "closing" and are kept open for 60 to 90 minutes. The holes are then closed, daubed with clay, and the cooling of the kiln allowed to proceed in the usual manner. The improvement is probably due to the discolorations being removed by the oxidising action of the air admitted.

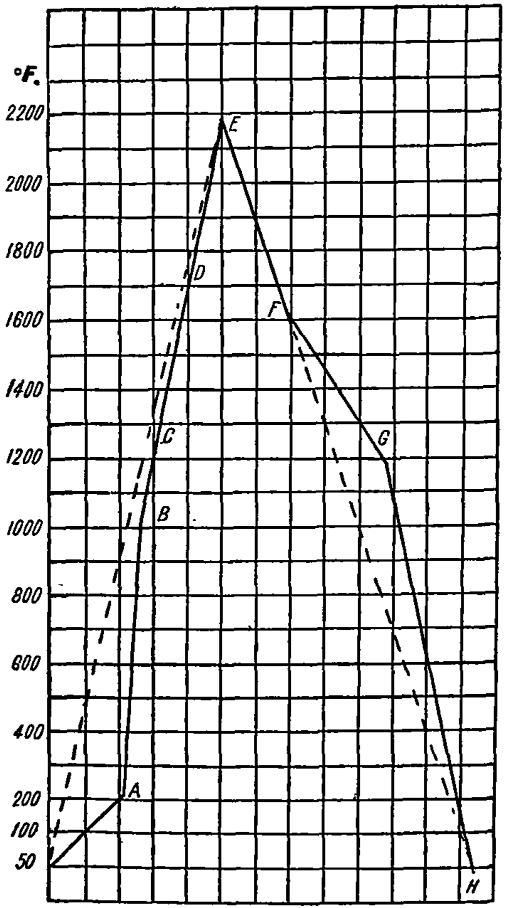

FIG. 84.—Time-temperature chart.

Annealing occurs during the period immediately after closing and in the earlier stages of cooling. Annealing, in the usual sense of the term, is not necessary with firebricks, as the requisite amount of annealing is easily obtained by merely allowing the closed kiln to cool naturally.

Cooling the bricks in the kiln is usually allowed to proceed automatically, the kiln being kept closed until the contents are sufficiently cool to be removed without any risk of their being chilled. In order to reduce the time required for cooling several methods are adopted: the chief of these are—

(*a*) Opening the damper leading to the chimney so that a slight current of air may be drawn through any leaks in the kiln. This is a risky procedure, as it tends to cause small currents of cold air to impinge on the goods.

(*b*) Openings may be made in the top of the kiln so as to allow the hot air to escape. There is little objection to this procedure.

(*c*) Openings may be made in the fireplaces, and the damper may be raised slightly so as to cause a gentle current of air through the kiln. This is risky, but is frequently done.

(*d*) Part of the wicket or doorway may be removed. This, though common, is very liable to chill the goods near the opening and to cause the formation of small cracks in them.

In cooling, especially at the higher temperatures, the greatest rapidity consistent with the durability of the goods should be attempted. It is now well recognised that each clay has a "danger zone," in which some of its constituents will tend to crystallise if they are maintained for a long time between certain limits of temperature. To avoid this it is well to study the cooling curves of the kilns made by means of a recording pyrometer—the danger zones of most fireclays lying between Seger Cones 010 and 1—and to arrange for the comparatively rapid cooling of the kilns whilst the danger zone is being passed. A slower rate of cooling may then be permitted in order to prevent the goods being "dunted" or cracked by too rapid a lowering of the temperature. The slower the cooling below 1000° C., the better it is for the goods.

During the earlier part of the cooling, some small amount of crystallisation may occur; this is particularly the case if the finishing temperature is above 1300° C., *i.e.* when sillimanite is formed.

Cooling defects are chiefly due to draughts of cold air impinging on the goods rather than to the actual speed of cooling, and many of these may be overcome by the somewhat paradoxical method of cooling with "hot air." That is to say, the kiln to be cooled may be supplied with air which, compared with the temperature of the atmosphere, is quite hot, but which, in comparison with the temperature of the goods in the kiln, is relatively cool, and yet is not sufficiently cold to produce any chilling or similar defects.

The cooling of the kiln requires considerable care and personal self-restraint, as there is always a temptation to effect it too rapidly and to open the kiln too soon.

The **drawing** of the goods from the kiln needs no description, beyond the statement that it should be done carefully and systematically so as to avoid damage. Bricks which adhere to each other may usually be separated satisfactorily by giving a sharp blow with a mallet or even with another brick.

Sorting is a highly important, yet much neglected, branch of firebrick manufacture. It is impossible to burn every brick in a kiln to exactly the same size, density, and hardness, and unless the bricks are sorted very carefully they will not prove wholly satisfactory in use. In most cases, it is sufficient to sort the bricks into three groups, but occasionally six groups are necessary.

Sorting is commonly regarded as a useless expense; this is a serious mistake, as the manufacturer who sorts his bricks with sufficient skill and thoroughness is in a far better position to secure the highest prices than one who endeavours to economise by avoiding sorting.

In addition to grouping the bricks according to their composition and the purposes for which they are to be used, the following are the chief groups into which bricks should be sorted:—

(*a*) Bricks exact to intended size.
(*b*) Bricks smaller than intended size.
(*c*) Bricks larger than intended size.
(*d*) Soft and under-burned bricks.
(*e*) Medium-burned bricks.
(*f*) Hard and over-burned bricks.

To some extent these groups overlap, but in practice no confusion is caused thereby.

Where great accuracy in size and shape are required, it may be necessary to grind the bricks with an abrasive wheel to exactly the correct dimensions. As the grinding destroys the dense skin on the surface, the face or end of the bricks which will be exposed during use should not be ground.

Storage.—When the bricks are drawn from the kilns they should be kept in rainproof sheds. Firebricks should never be allowed to get wet after they are burned, but should be kept absolutely dry until used, if their quality is to remain unimpaired. At many works in England, they are stacked out in the open and exposed to all weathers. This does not matter so much for the cheaper classes of bricks, but for higher-grade bricks it is a great mistake.

As showing the great importance to the manufacturer that his bricks should be properly stored before they are sold, unless they can be delivered direct from the kiln, it may be stated that even a single day's exposure to rain will lessen the strength of porous firebricks, as they are designed to withstand heat and not moisture, and so possess a structure entirely different from that of bricks intended for building purposes.

An elaborate series of tests on the effect of exposure to rain and wintry weather made by the author some time ago in the Northumberland and Durham districts shows that exposure to five days' rain without frost will reduce the strength of the bricks (as determined by crushing tests) to four-fifths their original value, and that a single night's exposure to frost of bricks previously exposed to rain or snow reduced their crushing strength to less than three-quarters of its normal value. This serious loss of strength is not appreciated by most makers of firebricks, if one may judge from the careless way in which they are left about on wet ground or without proper protection from the weather.

It is the custom to consider that firebricks are sold by their reputation—"the brand's the thing"—but this is only partially true, and not a few brickmakers might gain increased prices for their goods if they treated them properly after they had been withdrawn from the kiln.

The commonest cause of scum in firebricks is exposure to damp on an unsuitable foundation, and the peculiar "dead" ring of firebricks which have been exposed during a whole winter and then dried can scarcely fail to be noticed by anyone who cares to observe it.

Re-burning.—Some firms burn their best firebricks twice, selecting the best of those made in the ordinary manner, and re-burning these at a higher temperature. It is thought by the firms concerned that this method—as distinct from burning once at the higher temperature—produces bricks which are more resistant to corrosion, on account of the large proportion of vitrified matter present; but this is scarcely a complete explanation, as re-heating usually results in the loss of alkalies and silica and the formation of a more refractory material of somewhat lower mechanical strength. The chief advantage of re-burning the best firebricks lies in the facilities this method offers for sorting out the damaged and defective ones (thereby saving the cost of burning them at a higher temperature) and the cumulative effect of repeated heatings, which has an influence similar to that of a higher temperature acting for a shorter time.

A. Reynolds, in 1916, patented (Eng. Pat. 111,355) a method for increasing the refractoriness and the resistance to corrosion of fireclay goods by subjecting the working surfaces after the first firing to a temperature sufficiently high to produce incipient fusion. The bricks are embedded in the floor of a furnace with the working surface uppermost, and the spaces between are filled with some highly refractory material, such as chromite, plumbago, or ground carbon and tar. The furnace is then heated to produce the desired effect on the bricks.

Transport.—Fireclay bricks may be packed with a little straw in open wagons. It is usual to send a slight surplus over the quantity ordered, so as to allow for breakage in transit; but this is a matter of arrangement with the buyer. Fireclay bricks should be loaded and unloaded carefully; on no account should they be thrown into a truck or cart or tipped on to the ground. Such treatment damages the arrises, and makes it impossible to produce a structure highly resistant to slags, etc.

Properties of Fireclay Bricks.[1]—The properties of fireclay bricks are largely dependent on the clays from which they are made, though, as already explained, many of the properties are changed when clays are heated. Many desirable physical properties may be secured by suitable methods of manufacture, such as grading and proportioning the raw materials, suitable pressure in moulding, and a correct mode of burning.

The *surface* of fireclay bricks should be as level and smooth as possible, as irregularities form lodgments for corrosive dust, etc., and so lessen the durability of the bricks.

The *shape* of fireclay bricks must be as accurate as possible. They usually measure 9 inches by 4½ inches by 3 inches or 2½ inches, with a small allowance for the mortar, in order that two-header bricks may lie exactly on a stretcher when the wall is built.

The variations from the average or specified measurements should not exceed 2 per cent.; some specifications are even more stringent than this. The reason is that irregularly shaped bricks require more mortar and cannot be laid with thin joints; and as firebricks nearly always perish first at the joints, if these are irregular or if the bricks are laid carelessly, they do not form a durable structure. As the joints are more readily corroded than the brickwork, they should be made as thin as possible.

The criticism is not infrequently made that British firebricks are too irregular in size and, consequently, it is difficult to obtain good joints. Many of the Continental firebricks do not vary in length by one-thirtieth of an inch. To secure this great accuracy in size (i) the bricks must be made of accurately proportioned materials, shaped in a stiff-plastic or semi-dry state and properly burned; or (ii) the finished bricks must be ground accurately to size.

Variations in the size of bricks are chiefly due to: (i) variations in grinding the raw materials; (ii) changes in the proportion of water, grog, etc.; (iii) variations in the pressure; (iv) changes in the conditions of drying; (v) irregular burning; and (vi) unnoticed changes in the raw material.

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[1] A fuller description of the chemical and physical properties of clays and clay products is contained in the author's *Chemistry and Physics of Clays and Other Ceramic Materials* (Benn).

The retention of their shape and size after firebricks, etc., have been used for some time is highly important in some parts of furnaces, ovens, and other structures, and can best be secured by either burning the original bricks or blocks for a considerable time at a much higher temperature than that at which they will be used, or by making them of two or more materials so selected that the expansion of one neutralises the contraction of the remainder when the goods are in use. Semi-silica bricks are of this type.

The variation in shape is usually due to the following causes:

(i) variations in the proportions of the various materials used;
(ii) strains involved in the shape of the article;
(iii) variations in the rate and conditions of drying;
(iv) strains produced in the drying; and
(v) irregular heating and variations in the heating in the kiln.

Bricks may be *dressed* (*i.e.* ground accurately to shape) by means of a carborundum wheel, but care should be taken not to remove the skin from the face of the bricks.

The *changes in volume* which occur when refractory materials are heated are of two kinds:

(i) *Reversible changes*, which include (*a*) those common to most materials, *i.e.* expansion when heated and contraction when cooled; (*b*) inversion changes, *i.e.* changes in the crystalline structure causing an expansion or contraction—usually of a relatively large amount in a very short time; and (*c*) changes due to devitrification of the matrix or to solution of material in the molten glass.

(ii) *Irreversible changes*, which, if they occur on heating the material, do not revert on cooling. These may be due to: (*a*) decomposition of the material when heated; (*b*) the reduction in volume which usually occurs just before fusion; (*c*) the formation of gas, causing the material to froth or bloat; and (*d*) changes which have been stopped by cooling and so (for practical purposes) have been made permanent, though strictly they are reversible. There are many examples of such " arrested reactions " in the manufacture and use of refractory materials.

In practice, the manufacturer endeavours to complete the irreversible changes as far as practicable before selling the bricks, but as there is no absolute equilibrium attainable further heating always tends to a further change in volume. If this is within certain insignificant limits the result is regarded as satisfactory; otherwise the bricks are regarded as " underburned."

Both reversible and irreversible changes may occur simultaneously, but when the material is cooled to its original temperature only the permanent change in volume remains. Fireclay bricks expand slightly when reheated, the amount of expansion and the variations in the rate at which it occurs at different temperatures depending on the nature of the clay and on its previous treatment. Most fireclay bricks expand fairly rapidly between 500° and 600° C. The higher the temperature at which the brick was burned during manufacture, the more uniform will be its expansion on reheating. Firebricks which have been burned at 1410°–1550° C. do not show these irregularities in expansion, which appear to be chiefly due to cristobalite and to unaltered quartz.[1]

The following figures were obtained by Houldsworth and Cobb:[2]

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[1] See Houldsworth and Cobb, *J. Soc. Glass Tech.*, 1921, **5**, 16–43.

[2] *Loc. cit.*

EXPANSION AFTER PREVIOUS BURNING.

	Percentage expansion from 15° to 1000° C. after previous burning to			
	980° C.	1280° C.	1410° C.	1555° C.
Kaolin	0·36	0·53	0·48	0·44
Farnley fireclay	0·44	0·58	0·54	0·31
Glasgow fireclay	0·41	0·61	0·55	0·40
Ayrshire clay	0·43	0·61	0·56	0·42
Alumina	—	0·62	0·73	—
Magnesia brick	1·27	1·27	1·35	—

This expansion whilst hot must not be confused with the "after-expansion" mentioned in some specifications. The latter relates to a permanent increase in size which the bricks undergo when reheated, and which persists when the bricks are cooled, whereas the reversible expansion mentioned above disappears on cooling.

The *reversible changes* in volume in fireclay bricks are chiefly: (i) those due to free silica (p. 163), (ii) the normal expansion and contraction of burned fireclay.

The *permanent changes* (irreversible changes) in fireclays are chiefly included in the shrinkages which occur during the drying and burning; these may continue whilst the bricks are in use, especially if they have been underburned. At high temperatures the shrinkage due to gradual solution of the material in the molten glass may be serious; it is particularly noticeable when a slight pressure is applied, as in the refractoriness-under-load test. Some permanent change may also be due to the conversion of free quartz to cristobalite and tridymite.

Whilst the probable behaviour of a refractory material can often be predicted from a study of its change in volume and in its porosity when heated at different temperatures—the results of these observations being then plotted in the form of a temperature-porosity curve—the most accurate method is to heat a piece of material under conditions as nearly as possible similar to those under which it will be used and to measure the change in length. Such change is known as the *after-contraction* or *after-expansion*, though these terms are often restricted to the change which occurs when a piece of firebrick has been heated for only two hours at a temperature of 1410° C., as required by the Standard Specification of the Institution of Gas Engineers. A marked after-contraction in a fireclay brick indicates that it has been insufficiently burned.

The after-contraction of many firebricks when in use was a very serious difficulty to some furnace and oven builders a few years ago, and it then frequently happened that the linear after-contraction was as high as 3 per cent.; as most firebricks have been better burned during the last seven years, it is now usually much smaller and should in no case exceed 1 per cent. Except by the use of two or more materials—as in semi-silica bricks, which are not suitable for some purposes—it is impossible to eliminate entirely the after-contraction, as even when fireclay bricks have been fired a number of times, some contraction still occurs on re-heating them to the same or a higher temperature. It is possible to reduce it, however, by proper burning, to below 1 per cent., which is a negligible amount in most cases.

The average temporary expansion to 1300° C. is about 0·000006 per 1° C. It may be estimated by measuring the length of a brick when heated to a given temperature, and again when the brick has cooled to its original temperature; the difference is the temporary change in length. The total change in length when a brick or other article is heated to any given temperature is ascertained by making two fine saw-cuts parallel to each other on the face or front of the article to be tested, and either filling these with a dark-coloured pottery glaze or, as suggested by J. W. Mellor, fixing two fine platinum wires in them. The article is placed in the furnace or oven in which it is to be heated, and the distance between the two lines or the projecting ends of the wires is accurately measured by two cathetometers. When the brick or other article has reached the required temperature, the distance is again measured in the same manner, without removing the article. The difference between the readings shows the expansion or contraction which has occurred. If the article is then allowed to cool to the atmospheric temperature and the distance is again measured, the difference between the two measurements of the cold article—before and after heating—shows its after-expansion or after-contraction. In some cases where after-contraction occurs, the article may be shorter at the highest temperature of heating than at some lower temperature; this is the case when the temporary thermal expansion is masked by the after-contraction of the sample.

The *colour* of fireclay bricks is usually a pale buff, but many bricks have patches of brown and numerous black or brown spots on their surface. These are due to iron compounds present in the clay, the black spots being ferrous alumino-silicates formed from pyrite.

It is almost impossible to form a correct judgment of the refractoriness of a firebrick by its colour.

Sometimes the colour of the clay which has been heated to incipient fusion is changed during *cooling*. Thus, the well-known "flash" or reddish colour on certain fireclays is only produced when the clay is exposed to air, whilst still hot enough for some of the iron compounds to be oxidised. If pulled out of the kiln whilst still at their highest temperature, and cooled suddenly, such clays are buff with black spots, but if cooled very slowly, with an ample supply of air, they become reddish on account of the oxidation of the iron compounds which occurs.

The colour of burned fireclays is largely due to—

(*a*) The quantity of iron oxide contained in the clay.

(*b*) The other constituents of the clay accompanying the iron. See *Alumina*, *Lime*, etc.

(*c*) The composition of the fire gases during the burning.

(*d*) The amount of vitrification.

(*e*) The temperature at which the clay is burned.

It is a great mistake to suppose that the palest and most uniformly coloured fireclay bricks are the most valuable. On the contrary, the paler bricks have usually been fired at a much lower temperature than those which are more discoloured. In fact, the discoloration is itself a sign of a high finishing temperature. Bricks which have been so heated as to develop the iron spots must necessarily be capable of withstanding a similar temperature in use, whereas pale bricks which have not been so intensely heated have their refractoriness unproven, and may, for that reason, be regarded with more suspicion than the others.

Users of refractory materials are sometimes misled by small pieces of a dark, slag-like material on the goods, and regard these as signs of partial fusion. To a limited extent this is the case, but for most practical purposes these slag-like masses, unless unusually numerous, may be neglected; they result from the action of iron sulphide on the clay, and are generally so isolated as to have very little effect on the brick as a whole. Moreover, they usually occur most extensively at the surface, and an inspection of a broken surface will be much more favourable than that of surfaces ordinarily exposed.

The *texture* of firebricks is extremely important, as, next to being sufficiently refractory and of suitable chemical composition, the durability of the bricks depends chiefly upon their texture. Thus, fine-textured bricks will resist the action of slag or flue-gases longer than those of a more open and coarser texture, whereas if resistance to sudden changes of temperature is required, coarse-textured bricks would last longer. The texture is, therefore, more important than is often recognised by users of firebricks, and may vary from that required in bricks for insulating purposes to that required in bricks used for resisting acids. Hence, when ordering or supplying firebricks, it is very important that the purpose for which the bricks are to be used should be known to the manufacturer. Too fine or too coarse a texture is equally disadvantageous in the use of fireclay bricks, and the manufacturer must, therefore, modify the texture in accordance with the requirements of his customers. Where these are unknown it is only by chance that a manufacturer can supply suitable bricks.

Firebrick manufacturers tend to make bricks of too coarse a texture, as such bricks are less sensitive to sudden changes in temperature. For many purposes, however, as will be seen later, the finer the particles of a firebrick the greater will be its durability.

Coarse-grained firebricks are chiefly required where sudden changes of temperature occur frequently, as, whilst some fine-grained bricks are resistant to such conditions, they are not common. Fine-grained bricks are chiefly required where the bricks are liable to corrosion by acids, alkalies, molten fluxes, flue-gases, etc., though in all such cases the composition of the bricks plays almost as large a part as the texture. Provided the composition is suitable, a brick with a fine texture will be more resistant to corrosion than one with a coarser texture, as the former is less readily penetrated by molten material, and when larger particles are dislodged by abrasion, they leave much larger gaps and expose much more surface to further attacks than does a material composed wholly of small particles. For further information see p. 345.

The texture of firebricks is varied by the employment of one or more "grades" of fireclay and grog in the mixture and by the nature of the grinding process. If all the grains of material are very small, the resultant brick will usually have a very fine texture, whilst if particles of several different sizes or "grades" are used, the texture of the finished product will be correspondingly coarser. In any case, the particles should be angular and should interlock readily; this is very important, as bricks and other articles which do not possess an interlocking, granular structure are much weaker than others. No matter whether the structure is fine or coarse, it should be as uniform as possible, and where it is considered necessary to include an indefinite number of large grains or fragments in the bricks, these pieces should be scattered as uniformly as possible through the mass. Bricks in which relatively large fragments of rock or unground clay are irregularly distributed are frequently sold, but their quality would be greatly improved by making their texture more uniform.

The fractured surface of a fireclay brick should show no large holes, cracks, or other flaws, but the pores should be as uniform in size as possible.

A minute examination of the texture of a firebrick will frequently show distortions and strains in the material which are not so readily observed in any other manner. Such an examination is best made after the surface of the brick has been ground smooth, any fine dust removed by washing with water or even dilute hydrofluoric acid, after which a thin sheet of clear glass is cemented on to the surface by means of Canada balsam, as suggested by Lomas. The texture may then be examined with a lens or a low-power microscope.

The mineral constituents of well-burned fireclay bricks are mullite, quartz, tridymite or cristobalite and very small proportions of other minerals derived from the action of heat on the impurities in the clay. If the temperature has exceeded 1550° C. a little crystalline corundum may be formed, but only in the absence of magnesia, which, if present, would convert any free alumina into spinel. Some glassy matter is always present (see " Vitrification," *below*).

Usually the material is amorphous, and consists of irregular fragments cemented together by a small quantity of a glassy material; but fireclay bricks fired for a long time at a temperature above 1300° C., and cooled slowly, contain a few crystals of mullite ($3Al_2O_3.2SiO_2$). Prolonged or repeated heating is usually necessary for an appreciable quantity of these crystals to be developed. They may be seen more readily if some of the amorphous material is removed by treatment with hydrofluoric acid. Strictly speaking, fireclay bricks cannot be regarded as fully burned until all the alumina has been converted into mullite, any surplus silica into tridymite (or cristobalite), and all the fluxes have been saturated with either silica or alumina or both. In practice, however, this state of affairs is never reached. The development of refractory materials consisting almost wholly of mullite has been very considerable during recent years. Further details are given on pp. 385–390.

The factors of chief importance [1] in relation to texture are:

(i) the grain-size of the clay;
(ii) the nature, proportion and grading of the grog or other non-plastic material; and
(iii) the conditions under which the bricks or other articles are burned.

Vitrification.—The amount of vitrified or glassy material in fireclay bricks is larger than is commonly supposed, and consequently the use of such bricks at or above 1500° C. is restricted. This difficulty is avoided, to some extent, by the addition of alumina (see Chapter V.), or the use of a material of the sillimanite group (p. 146), the clay being used chiefly as a bond.

The *hardness* of fireclay bricks varies greatly; some are so soft as to crumble when the blade of a pocket-knife is applied to them, whilst others are harder than steel. The hardness appears to increase rapidly as the finishing temperature is raised, and is lowest in underfired bricks.

The hardness may be tested by means of a Brinell ball or Shore scleroscope, the former giving more concordant results. For the Brinell test a piece of thin foil about 2 inches square should be placed on the clay or article to be tested, and a standard Brinell ball made of hardened steel and measuring exactly 10 mm. in diameter placed on the foil. A steady pressure (preferably hydraulic) of 500 kg. or 1·102 lb. is then supplied to the ball for 30 seconds, after which it is released, the ball removed and the depth or diameter of the indentation measured. The hardness is then found from a table supplied with the instrument or calculated from the formulæ

$$H=\frac{P}{1{\cdot}5708D(D-\sqrt{D^2-d^2})} \quad \text{or} \quad \frac{P}{3{\cdot}1416De}$$

where H=the hardness number, P=the pressure applied in kg., D=the

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[1] J. W. Mellor and A. T. Green, *Chem. Ind.*, 1938, **57**, 636.

diameter of the sphere, d=the diameter of the indentation, and e is the depth of the indentation and is equal to $\frac{1}{2}(D-\sqrt{D^2-d^2})$.

The *true porosity* of a fireclay brick includes (i) the open pores, which can be filled by immersing the brick in water (see *apparent porosity*); and (ii) the sealed pores into which no water can enter. The volume of these sealed pores can only be ascertained by indirect methods.

The true or total porosity varies with the temperature at which a brick has been burned. It often diminishes during the earlier stages of burning, but increases as the temperature rises above 1140° C. (Cone 3*a*). The *apparent porosity,* which is due to the open pores, on the contrary, tends to diminish, because as the temperature rises and the heating is prolonged, these open pores become filled with fused material. The sealed pores are, in part at any rate, due to the formation of gases during the burning of the bricks, the material in which they are produced being too viscous to permit the bubbles to escape.

The *apparent porosity* of firebricks is usually measured by weighing the amount of water absorbed when the brick is immersed for several hours. The exterior of a fireclay brick is usually composed of smaller particles than the interior, and a whole brick is, therefore, less porous than a portion from which the outer surfaces have been removed. For this reason, it is important, in considering the porosity of fireclay bricks, to know whether this term is applied to whole or to broken bricks. The test is made by immersing the article in water,[1] wiping off the excess of liquid after some time, and weighing the article. Its increase in weight is understood to be due to the water absorbed by the pores, and the volume of the latter may be calculated from the weight of water thus retained on the assumption that 1 oz. of water measures 1¾ cubic inches, or 1 c.c. of water weighs 1 gramme. A very rapid test of porosity is to hold the tongue in contact with the brick. If a distinct suction is felt, the brick is very porous. If there is no distinct suction but the water is absorbed rapidly, it is moderately or slightly porous.

Although it is the usual practice to express the porosity in a unit of *weight,* it is more correct to express it in terms of *volume,* and the figures representing the porosity of an article should indicate the volume of the pores it contains in relation to the total volume of the article itself. This volume may be directly calculated (in the case of a brick by multiplying the length by the breadth by the depth). It may also be determined by finding its loss in weight when suspended in water by means of a fine thread from one arm of a balance, then

$$\text{Porosity}=\frac{\text{weight when soaked in water}-\text{weight when dry}\times 100}{\text{loss in weight when suspended in water by a thread}}.$$

The amount of porosity in a fireclay brick is very important in some industries, as, the more porous the brick, the sooner will it succumb to the corrosive or abrasive action of dust, furnace contents, fluxes, and other materials with which it comes into contact. On the contrary, highly porous bricks will suffer much less than denser ones when subjected repeatedly to sudden changes in temperature. It is, therefore, necessary to consider which of these properties is the more important in a particular case, and to regulate the porosity of the bricks accordingly.

In consequence of this dual characteristic, the porosity of (whole) fireclay bricks varies from about 8 to 24 per cent. by volume.

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[1] Carbon tetra-chloride has been suggested as preferable to water; being a much more mobile fluid, it penetrates the smaller pores more readily and enables porosity tests to be made more rapidly.

The porosity may be increased by adding (i) kieselguhr, or (ii) sawdust, peat, or similar combustible material of such a nature that it burns away completely, leaving air-spaces or pores in its place. The materials are mixed together in a dry state, and then sprinkled with water, turned over with spades, and afterwards pugged so as to form a paste; the bricks, blocks, or slabs are then moulded, dried, and burned as described on p. 277 *et seq.*

The addition of a little sulphur sometimes increases the porosity of firebricks, but more usually it combines with any lime and alkalies present, and forms a slightly vitrified material highly resistant to acids. In consequence, the addition of sulphur is sometimes made to fireclays which are to be used for acid-resisting or chemical ware.

The changes in porosity after the brick has been re-heated several times is generally a good criterion as to its capability to resist a load at a high temperature. Most bricks which are capable of withstanding a pressure of 40 lbs. per square inch at 1350° C. show only very slight changes of porosity when heated to a temperature of 1425° C., whereas bricks which are weaker at 1350° C. usually show more marked changes in porosity when re-heated. The porosity of a brick capable of withstanding the pressure just mentioned should not decrease more than 5 per cent. on re-heating to 1400° C.

Similarly, the changes in porosity of a brick after being re-heated to various temperatures and then allowed to cool, when plotted in the form of a graph afford a useful means of predicting its behaviour after being heated to intermediate temperatures and then allowed to cool. As the porosity diminishes the strength of *cold* bricks usually increases—the large amount of vitrified matter forming a stronger bond—but the strength of *hot* bricks is reduced because vitrifiable matter is a source of weakness at high temperatures.

The *apparent* density or volume-weight of a firebrick (which includes the pores) may be determined by dipping the brick into molten wax or similar material in order to apply a very thin coating which will render the brick impervious without otherwise affecting the results. After it has regained its original temperature, the brick should be suspended from a balance by a thin wire and accurately weighed, after which it is completely immersed in a vessel of water and again weighed. The weight of the brick suspended in air divided by its loss when suspended in water is the *apparent density.*

The apparent density is reduced if sealed pores are present.

In calculating the volume occupied by fireclay bricks, an assumed apparent density of 1·9 to 2·0 will usually be correct. By the addition of combustible matter it is possible to reduce the apparent density of the bricks to 1·0, the porosity being then 50 per cent. by volume; such light bricks are extremely poor conductors of heat, and are correspondingly valuable for some furnaces.

The volume-weight of a clay at the close of the second stage of firing is less than at the beginning. Measurements of it represent a balance due to the replacement of water and carbonaceous matter by the air and the shrinkage of material, and are of little value.

The *true* specific gravity can only be found by grinding the material so finely that the individual particles contain no sealed pores, and then determining the specific gravity of the powder. The specific gravity of fireclay bricks is usually about 2·6, but is rather lower if any sand has been added in process of manufacture. A less accurate result may be obtained by suspending the brick as described above, and weighing it first in air and then in water and calculating as before. The inaccuracy inherent in this method is due to the fact that some bricks contain a considerable proportion of sealed pores into which water cannot enter. The result obtained by this method is preferably termed the *apparent specific gravity.*

The *composition* of fireclay bricks bears a close resemblance to that of the clays from which they have been made, but the firebricks show no "loss on ignition," and usually contain a slightly less equivalent of potash and soda. The composition of different firebricks varies greatly, and the figures given in Table LIX. are only approximate.

The details of the chemical composition of firebricks are usually of less value than their physical properties, though where bricks are required to resist the action of the acids, bases, fluxes, or gases which can enter into chemical reactions with them, the chemical composition is of much more importance, and should, in such cases, be carefully considered.

TABLE LIX.—COMPOSITION OF FIRECLAY BRICKS.

Source of Material.	Silica.	Alumina.	Ferric Oxide.	Lime.	Magnesia.	Potash and Soda.
Stourbridge . .	73	23	2·4	0·5	0·5	1
Newcastle . .	63	31	1·7	1·5	0·7	2
Pensher . . .	65	30	2·0	0·5	0·5	2
Flintshire . .	88	4	6·0	1·2	..	..
Leeds . .	77	19	1·4	0·5	0·6	1
Elland . . .	62	35	1·2	0·7	..	1

The *acid character* of fireclay bricks is not appreciable unless the bricks are at a high temperature, but it is then found that they combine with alkalies (soda, potash, etc.), other bases (lime, magnesia, iron oxide, ash, etc.), or salts (chlorides, sulphates, and carbonates) at a rate which depends on their porosity.

The compound formed is usually a mixture of fusible aluminates and silicates with some alumino-silicate.[1] Thus, lime forms calcium aluminates and silicates, iron oxide is dissolved and forms a fused ferrous or ferric silicate. Coal ash (flue-dust) forms a mixture of each of the above with various other silicates.

In the presence of soda, fireclays can form crystals of nephelite ($Na_2O.Al_2O_3.2SiO_2$), and in the presence of potash, leucite ($K_2O.Al_2O_3.2SiO_2$). These crystals are identified by their low refractive index and their weak birefringence.

Clays and silica are such powerful acids that at high temperatures they turn out the acid radicle from various salts, forming a new salt (alumino-silicate or silicate), and setting the hydrochloric, sulphuric, or other acid free —usually in the form of a gas.

When combination occurs between a firebrick and a flux, heat is evolved; this sometimes raises the temperature locally to above the fusing-point of the compound, and so increases the amount of fusion or "corrosion" of the bricks.

Bricks with a close texture can withstand the action of bases and alkalies for considerable periods, but porous bricks are rapidly attacked and destroyed.

It is well known that chemical reactions proceed more rapidly when the materials are in a fine state of division, so that it would appear as though

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[1] Some investigators consider that when alumino-silicic acid (clay) is decomposed on heating, a mixture of free alumina and silica is formed. The experimental evidence on this matter is not yet complete.

coarse-grained bricks would better resist the action of bases and alkalies. In this connection, it is necessary to remember, however, that a coarse-grained texture will usually be accompanied by a high degree of porosity, and the latter will seriously detract from the good effect of the former. Hence, a brick whose exterior is of fine particles well compacted, will frequently last much longer than a brick made of much coarser particles, though if two bricks are of equal porosity, the one made of coarser grains will have the greater resistance to chemical action.

In considering the resistance of a firebrick to chemical action, it is important to remember that the effect of certain substances may easily be overlooked. Among these are dust from the fuel used in heating the furnace, volatilised alkalies and alkali-salts, etc., all of which tend to reduce the refractoriness of any firebricks with which they come into contact. The action of these substances, as well as that of slags, etc., must now be considered.

The *resistance to slags* and other so-called corrosive materials, which is a desirable characteristic of some fireclay bricks, is due to the closeness of their exterior rather than to the chemical composition of the bricks. As explained above, fireclay bricks are essentially of an acid character[1] when sufficiently heated, and they must all in time be attacked and destroyed by any material of an alkaline or basic character which comes into contact with them. The extent to which combination of these materials with the bricks occurs depends chiefly on the temperature and on the amount of each material which comes into direct contact with the other. If both materials are in a coarse state of division the area of contact will be small; if both are in fine powder the action will be much more rapid. If the base is in the form of a liquid (as slag) it will penetrate any coarse pores in a brick and break down the brick far more rapidly than if the surface were more dense and compact.

The first general result of corrosion by slag is for some of the refractory to be dissolved by the slag. This increases the melting-point of the slag, so that further corrosion becomes less and less as the slag becomes more and more viscous, though the action may never cease. An increase in the temperature of the slag or bricks greatly increases the corrosion under normal circumstances, because it makes the molten slag more fluid and so permits it to dissolve more brick material. The movement of the slag also increases corrosion by increasing the amount of contact between the slag and the brickwork. Bricks with a high porosity also increase the corrosion for the same reason.

Experiments by Hirsch and others have shown that when blocks of slag are laid in hollows cut in firebricks, the most resistant bricks were those made of finely ground clay which had been mixed with as little water as possible.

Hirsch has found that cupola slags penetrate firebricks chiefly by mechanical action, but Portland cement has a strong corrosive action on them, and dissolves alumina and silica from them to form new compounds with a composition corresponding to the formula $2{\cdot}5CaO.Al_2O_3.3SiO_2$. (It should be noted that Rieke[2] has shown that this is the most fusible calcium aluminosilicate of the $xRO.Al_2O_3.3SiO_2$ series, and that its formation would be expected from the general laws of fused substances.)

Slags which contain sodium or potassium carbonate or nitrate are particularly corrosive. A mixture of sodium and potassium carbonates with finely ground firebrick will produce a completely fused mass at about 950° C.

The corrosive action of slag on powdered firebrick is much greater than

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[1] The prevalent idea that fireclay bricks are neutral is erroneous.

[2] Table XXII.

that on the bricks themselves, owing to the great amount of surface exposed. Howe, Phelps, and Ferguson,[1] who made tests on powdered bricks, found that whilst a high alumina-content usually lessened the corrosion by slag, this was not invariably the case.

Firebricks burned at very high temperatures have a greater resistance to corrosion by slags. Those bricks in which quartz grains are used to reduce plasticity are strongly attacked by Portland cement, but only slightly by cupola slags. The corrosive action of whiting (calcium carbonate, which forms lime at 700° C.) is the same as that of Portland cement, but is more intense. The fused calcium aluminates, silicates, and alumino-silicates produced by the action of lime compounds on firebricks appear to form a protective coating which prevents further action so long as the temperature of the bricks is not notably increased. This is partly due to the formation of an alumino-silica slag of increasing richness in silica, and, consequently, more refractory than the material first formed. This slag enters the brick and begins to attack and dissolve fireclay, with the result that its temperature of fusion rises. It may happen that by the time the pores of the brick are filled with slag, or with a combination of fireclay and slag, the point of fusion of the complex mass is higher than the furnace temperature. Usually, however, the effect of the slag penetrating the brick is to make the latter more fusible. Thus, in an instance observed by G. Rigg, a firebrick which had been used for three months in a furnace working at 1250° C. to 1350° C. had its softening-point reduced from 1700° C. to 1400° C., and shortly after this the brickwork collapsed.

The apparent anomaly that a slag may either increase or reduce the fusibility of a brick is due to the formation of two kinds of silicate. If meta-silicates ($RO.SiO_2$) are present in the slag the alumina dissolved out of the firebrick will make the slag still more fluid, but if the slag is rich in other silicates ($2RO.SiO_2$), the solution of alumina raises the melting-point and stiffens the slag. This is clearly shown by some experiments of G. Rigg, which are summarised in the following table:—

TABLE LX.—EFFECT OF ALUMINA ON FUSIBILITY.

$CaO.SiO_2$.			$2CaO.SiO_2$.		
Al_2O_3 Per Cent.	Fusion-Point.	Character.	Al_2O_3 Per Cent.	Fusion-Point.	Character.
..	1460° C.	Stiff	..	1382° C.	Stiff
6·8	1318° C.	Fairly liquid	6·8	1422° C.	Very stiff
13·3	1296° C.	Very liquid	13·3	1468° C.	„ „
19·6	1272° C.	„ „	19·6	1453° C.	„ „

With most, if not all, slags, the vigour of the action on fireclay bricks appears to be a function of the temperature. Some slags will lie in contact with the fireclay mass, when just above their melting-point, without any serious degree of combination taking place. At a higher temperature, however, the vigour of the attack will increase. The absorption of the fireclay by the slag, as the temperature rises, causes the slag to become more viscous, and creates the apparent anomaly of the slag stiffening with a rise of temperature.

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[1] *Journ. Amer. Cer. Soc.*, 1923, **6**, 589.

When the slag occurs on the hottest surface of a refractory mass—as is the case with a blast-furnace lining—the destructive effect is not usually so marked as when the slag occurs on a cooler surface—as in a retort or muffle. Under the former conditions the slag, as it penetrates into the brick, meets with a falling temperature and soon solidifies, while under the latter the slag, as it penetrates, meets with a rising temperature, and its destructive effect is enhanced.

One of the most important means of resisting the action of slags consists in providing the bricks with a good " skin." This is formed automatically by the pressure, exerted in shaping the bricks, forcing some of the water to the surface, carrying some of the finest clay with it, and leaving this as a thin but very dense deposit on the surface. The resistance of this skin to corrosive agents is very remarkable. Its absence should be regarded as a sufficient reason for rejecting a brick to be used under conditions where corrosion is anticipated.

When the importance of this skin is remembered it will be obvious that tests on fractured bricks are useless for ascertaining their resistance to slags.

The effects of slags on fireclay bricks appear to be due to:

(*a*) mechanical abrasion or *erosion*;

(*b*) solution of portions of the firebrick in the molten slag; such solution may be physical or it may be the result of chemical action—often described as *corrosion.*

Frequently both these effects occur together or immediately after one another, and in many cases the erosion is more serious than the corrosion. Sometimes a slag dissolves the matrix surrounding the particles of grog in a firebrick, and when the latter " float away " in the slag the space left offers a large surface for rapid corrosion.

The extent of the erosion and corrosion depends upon: (i) the rate of formation and of removal of the product formed by corrosion, (ii) the rate at which the slag is supplied, and (iii) the nature of the refractory material. If the removal of the product is rapid, with consequent exposure of fresh surfaces, the destruction will be correspondingly rapid. If, on the other hand, the product is highly viscous, the rate of destruction may be low. A small difference in the temperature or the composition of the slag may make a great difference in its viscosity and rate of attack.

The solubility of various firebricks and silica bricks in acid slags has been determined by R. Fehling,[1] who has found that the maximum solubility (attack) of the bricks occurs in bricks with 10–40 per cent. and 60–80 per cent. of alumina, and that the bricks having the greatest resistance to slag contain approximately 50 per cent. of alumina. Pure silica and pure alumina are both highly resistant to acid slags, but a very small proportion of impurities greatly reduces the resistance and increases the solubility of the brick in the slag.

In all bricks which have been penetrated and attacked by slags there is a series of different zones or layers, commencing with the outermost zone of unaltered slag (or slag-forming material) and ending with the unaltered brick. These layers may appear to be quite distinct, but a sufficiently close examination with a microscope will show that intermediate materials are also present and form transition zones. Thus, in the case of a fireclay brick attacked by coal ash, the outer zone of slag is usually very thin at high temperatures, but thicker at lower ones; it usually contains albite or

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[1] *Ber. deut. ker. Ges.*, 1938, **19**, 498.

anorthite (lime felspar) (p. 90), iron oxide, and some crystals of mullite. The second zone contains more mullite crystals. The third zone consists mainly of firebrick penetrated by slag and shows the commencement of the reaction between the two materials. The last zone is the unaltered brick.[1]

In the most highly corroded portion of fireclay bricks attacked by slags, the zone of corrosion is composed chiefly of lime felspar (anorthite), iron silicates and mullite crystals, with iron in solid solution in the " glass." The destruction is serious because (as explained in the 28th *Report of the Institute of Gas Engineering*, 1937) 1 part of lime will remove 1·82 parts of alumina and 2·14 parts of silica from the brick to form the anorthite. Probably 1 part of lime will destroy at least 4·2–4·5 parts of firebrick, and may indirectly destroy much more.

Silica bricks are less severely attacked because anorthite is not formed. Bricks richer in alumina than is fireclay, especially those containing much mullite, show little slag on the surface, but may show much penetration of slag and a noticeable proportion of corundum and mullite crystals.

Siliceous bricks tend to be dissolved readily by basic slags. The crystals in the outer zone formed are mainly cristobalite, those in the second zone are chiefly mullite, and there is usually a definite penetration of molten glass (slag) into the brick. Some slags dissolve free silica from fireclay bricks in preference to attacking the fireclay.

The extent of corrosion depends partly on the composition of the slag and on that of the clay in contact with it. A study of the equilibrium diagram of the lime-silica-alumina system will show that bricks containing a low proportion of alumina must behave differently towards slags from bricks rich in alumina on account of the different fields occupied by the mixtures. With firebricks low in alumina the tendency is to form an anorthite-silica-wollastonite complex melting at 1170° C., whereas highly aluminous bricks tend to form a corundum-anorthite-mullite complex which does not fuse below 1500° C., though with ample slag another kind of complex fusing at 1200° C. may be formed. It is also significant that the glassy (vitrified) matter in fireclay bricks is much more corrosive in its effect on the remainder of the firebricks than is the case with the vitrified material in silica bricks, as the latter consist chiefly of crystalline material.

The action of slags is largely dependent on the physical nature of the bricks. For instance, slag does not penetrate readily into a brick made wholly of clay unless the latter contains fine cracks. The addition of grog reduces the tendency to cracking, but it tends to permit more penetration of slag by increasing the permeability of the mass. A brick made of fireclay and coarse grog is more resistant to slag than is a brick made of coarse clay and fine grog.

The intensity of corrosion is much greater with " thin " mobile fluids than with more viscous ones. Hence slags high in lime are highly corrosive, especially if they also contain iron and manganese compounds. In other words, the " better " (*i.e.* the more mobile) the fused slag from the metallurgist's point of view, the greater is its corrosive action on the furnace lining.

For *comparing the effect of slags* or of the same slag on different bricks several methods have been devised. The most important of these are:

(i) A cylindrical hole 1 in. in diameter and 1 in. deep is drilled in the

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[1] McDowell and Lee, *J. Amer. Cer. Soc.*, 1928, **11**, 35; McVay and Hursh, *ibid.*, 1928, **11**, 224; and others.

face of a brick and is filled with powdered slag. The brick is then heated under prearranged conditions. When cool the brick is sawn vertically and the penetration of the slag is noted. The objection to this method is that it ignores the protective action of the skin of the brick.

(ii) A moulded cylinder of the slag is laid on the upper face of the test brick and heated to a prescribed temperature (1400° C.) for a definite time. The cold brick is sawn through vertically so as to expose a section of the centre of the slag-pool, and the width and depth of penetration are noted. Thin sections may also be examined under the microscope so as to gain further information as to what changes have occurred and what crystalline and other products are formed. The production of anorthite (lime felspar) and mullite is especially significant.

(iii) The test bricks are heated to a prescribed temperature (1400° C.), and a weighed amount of powdered slag is blown through the gas-burner on to the face of the bricks, on which it impinges at an angle of 45°. After maintaining the temperature for (say) half an hour, the bricks are allowed to cool and they, as well as any "drops" of adherent slag, are examined microscopically. The drops are usually rich in anorthite.

(iv) Weighed proportions of finely ground brick and slag are made into cones and their refractoriness is determined. Thin sections of the heated cones are also examined microscopically.

(v) Complete melts of mixtures of slag and brick in known proportions are made and the products are examined.

When comparing the behaviour of various bricks with slags, it should always be remembered that the slag used in experiments seldom represents that formed under actual conditions of use. If a fully matured slag is employed for the tests, the results will have little or no relation to works' conditions, yet if the raw materials composing a slag are used the result is liable to be equally unreliable. Fromm[1] has found that the ordinary 2-hour test at 1400° C. is not nearly sufficient for ascertaining the true resistance to slag. A higher temperature and a longer duration are needed. The difference in attack at 1450° C. after 6 hours' heating is usually very much greater than that at 1400° C. after only two hours' heating. Hence observations of the effect of slags under actual conditions of use are of far more value than most laboratory tests, though the reactions involved are then so complex that simulative tests are, at present, of limited value.

The effect of slags may clearly be reduced by using bricks with a fine uniform texture, free from fissures or large pores, so that all destruction is confined to the surface. In much of the refractory material on the market, however, the mass is not uniform; it contains numerous fissures and large pores, and consequently irregular penetration is frequently observed. In this, as in many other cases, the reactions which occur are so largely conditional on factors which may easily be overlooked, that the true nature of the reaction itself, and the conditions which are favourable or opposed to it, are seldom easy to ascertain in detail. Coals containing salts, when used in the manufacture of illuminating gas or coke, have a corrosive action upon fireclay bricks and retorts, especially when iron compounds are also present in notable proportions. The higher the temperature of the oven or retort the greater is the activity of the salts in the coal. W. J. Rees has suggested that the presence of salts causes an increase in the absorption of iron compounds by the fireclay, causing the formation of layers of hæmatite and resulting in spalling.

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[1] *Ber. deut. ker. Ges.*, 1934, **15**, 49.

Resistance to flue-dust is often an important property in fireclay bricks, and deserves more consideration, as it may be very important to choose bricks which are capable of withstanding the action of flue-dust under the conditions to which the bricks are subjected during use. The commonest flue-dust is derived chiefly from the ash left by the combustion of fuel, and at the high temperature at which it comes into contact with the firebrick it readily adheres and forms a fusible mixture of silicates and alumino-silicates, the composition of which depends on that of the flue-dust, which thus behaves like a base in its action on fireclay bricks.

Some fireclay bricks are not attacked by coal ash when they have been properly made and burned, but other bricks—made from the same clay but by a less skilful man, or produced from improperly graded materials and containing too much coarse grog, or which have not been sufficiently burned—are irregularly penetrated by the ash or dust. Flue-dust containing sodium salts appears to attack the bricks very greatly on the surface, though the penetration is comparatively small. *Alkaline vapours* act in a similar way to flue-dust, but more intensely, and may also effect the conversion of quartz into a form of silica of lower specific gravity, such as tridymite or cristobalite. Flue-dust penetrates more readily into bricks made of some fireclays than into silica bricks, and, according to Mellor and Emery, in such cases the bond is generally attacked before the coarser grains. Uniformly grained bricks are recognised as being generally the best for resisting the action of flue-dust.

Mellor and Green[1] have found that fireclay test-pieces heated to 1200°–1350° C. in the presence of potassium chloride vapour expand uniformly in all directions, the increase in volume being 9 per cent. in some cases.

Most firebricks increase in size and weight on exposure to salt vapours at 1000° C. Sillimanite behaves similarly, but silica bricks are less affected than fireclay bricks.[2]

Although the action of salt derived from coal may be very injurious to fireclay bricks at temperatures above 800° C.—particularly when the latter are used for coke-oven walls—the damage is limited by the surface of the bricks rapidly becoming covered with a glaze formed by the action of the salts on the clay, whereby the subsequent rate of corrosion is greatly diminished. If, however, the glaze is sufficiently fluid to drip away, the corrosion is more rapid. By subjecting the bricks to a treatment or to conditions whereby the salt should not come into contact with them until the temperature is sufficiently high (about 1200° C.) to form a glaze which fuses on the surface without penetrating the bricks, in a similar manner to salt-glazing, the bricks will be much more durable than when they are subjected to the action of salty vapours at temperatures below that at which the glaze forms rapidly on the surface. The difference is due to the fact that, at a lower temperature, the salt penetrates the pores of the brick, forming complex silicates and effecting chemical alterations in the substance of the brick, which result in changes in the coefficient of expansion and contraction of the various constituents, so that the different parts of the brick expand and shrink differently and soon begin to disintegrate. When the action of the salt is confined to the surface of the bricks, however, no such general disintegration can occur. Moreover, on prolonged heating, the glaze tends to dissolve more alumina and silica, and so forms a less fusible and more resistant covering.

Mellor and Emery have obtained some surprising results by dropping finely-divided powders on to firebricks whilst the latter were being heated in

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[1] *Chem. Ind.*, 1938, 57, 633.

[2] *Trans. Cer. Soc.*, 1937, 36, 217–225.

a small test furnace. The results are by no means conclusive, and possibly are not comparable to ordinary conditions of use, but they seem to show that the flue-dust from boilers has a very active corrosive and penetrative effect on ordinary firebricks; retort-dust is not quite so active, whilst finely-divided oxides of copper, zinc, and iron in a highly reducing atmosphere have a high penetrative power at unexpectedly low temperatures—copper at 600° C., iron at 1100° C. The dust from the slag chamber of steel furnaces is also very active, but tap-cinder dust appears to be the most actively corrosive of the dusts examined.

The composition of the dust is by no means the sole factor which determines its distinctive action; for instance, basic slag may penetrate deeply yet be very feebly destructive, whilst lime—which does not penetrate nearly so easily—has a far greater corrosive action, and is, therefore, more harmful to the bricks.

For obvious reasons, the state of the atmosphere in the interior of the furnace, oven, or kiln also determines the effect of the dust on the bricks, as some substances, such as " bull dog " dust or iron oxide, are not appreciably corrosive in an oxidising atmosphere, but under reducing conditions they form complex ferrous silicates which are highly corrosive fluxes. Hence, ferruginous dusts in reducing atmospheres are characterised by the rapid production of slag from the fireclay, this being the cause of the steady drip of slag which takes place on the bottoms of retorts heated by producer gas from a coal with a ferruginous ash.

Resistance to the action of flames and gases is very necessary where bricks are used for the construction of flues, furnaces, etc. It has been shown by several investigators that carbon monoxide—a gas produced by the imperfect combustion of coal, and a constituent of producer gas and of many flue-gases—is decomposed by some hot fireclay bricks with deposition of carbon. Various hydrocarbon gases are also decomposed in the presence of hot fireclay bricks and deposit carbon (see *Deposited Carbon*).

Methane (CH_4) can completely disintegrate some fireclay bricks, and coal-gas under some conditions has a similar action. In both cases the effect is attributed to minute particles of (reduced) iron in the bricks.

Ethylene is also decomposed, above 360° C. in the presence of iron or above 600° C. without iron, but it then only discolours firebricks and does not form the voluminous deposit characteristic of carbon monoxide.[1]

Curiously enough, coal-gas causes no cracking or disintegration unless the carbon dioxide has been removed[2]; then the attack at 800°–900° C. is very pronounced, and disintegration, cracking, and carbon deposition occur. Moist coal-gas has no effect. The inhibiting effect of carbon dioxide may be due to its forming carbon monoxide with the carbon; this reaction proceeds more rapidly at 850° C. than the reverse reaction.

A somewhat parallel instance of destruction by gas is afforded by the blast furnaces used for ores containing zinc. Under these conditions the vapours of metallic zinc are liable to enter the bricks and, passing to the cooler parts of them, to oxidise at the expense of the CO_2 and solidify. The veins of crystallised zinc oxide which result from this action have a powerful effect in rupturing the brick and causing crumbling.

Speaking broadly, the action of gases is only appreciable on porous bricks. Those which have a dense skin offer so much resistance to the entrance of the gases that little or no action can occur. A compact outer surface is, therefore, the best protection against the action of gases.

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[1] *Inst. Gas Eng.*, 28*th Rep. Refract. Matls. Committee*, 1937, pp. 11–13.

[2] *Inst. Gas Eng.*, 28*th Rep. Refract. Matls. Committee*, 1937, pp. 13–21.

Volatilisation of some of the materials which are being heated may produce vapours which, when they condense, frequently have a markedly corrosive action on refractory goods. The volatilisation of alkalies and of salts—such as sodium chloride—whose acids are feebler than that of clay, and are therefore decomposed by the fireclay bricks—are two striking instances of volatilisation increasing the fusibility of firebricks.

Sulphur in the fuel burns to sulphur dioxide, and in the presence of air and steam this is converted into sulphuric acid, which may have a corrosive action on the clay goods. To some extent, this sulphur may be prevented from volatilising by mixing slaked lime with the coal, but this is seldom practised for obvious reasons. It is extremely unwise to do so, as it makes the coal clinker excessively, and, with care in burning, both clay and silica are unaffected by sulphuric acid to any appreciable extent. Moreover, the results of many of the author's observations tend to show that the richer a fireclay is in alumina the greater will be its resistance to the products of the sulphur in the fuel. The presence of sulphur inside gas-retorts is of less importance than it is in a furnace, as the lower temperature reached in the retorts and the absence of air prevent any serious quantity of sulphuric acid being formed in a free state.

Wet Fuel is far more serious than sulphur, as superheated steam has a strong softening effect on fireclay work, especially when the latter is porous. The proportion of moisture in ordinary coal is not sufficient to do much harm, so far as the furnace is concerned; the carbonaceous lining of a gas-retort after a short time of use protects the latter from serious damage, so that unless the fuel is abnormally damp no special precautions need be taken. A careful study of the firebricks used in boilers having a steam jet in the fire-box to increase the draught will soon show the effect of heating fireclay in presence of an excess of steam, but this effect is so seldom noticed in the manufacture of gas as to be scarcely worth the attention of the gas engineer, though the fact that, under certain conditions, steam may seriously affect the durability of the retorts and brickwork should be kept in mind.

Deposited Carbon.—The internal strains set up in firebricks when carbon is absorbed within the pores of the material have not been sufficiently studied to render any publication of definite results satisfactory. It is well known that hydrocarbons and carbon monoxide are decomposed by fireclay, leaving much of their carbon behind and very noticeable changes in the strength of the fireclay body taking place, though the exact nature of these reactions remains unknown. In some ways, the action appears to be catalytic, and to be due to ferric compounds (*iron spots*) or to metallic iron produced by reducing gases from the iron compounds in the fireclay. The ferric oxide is reduced to ferrous oxide or metal,[1] which acts as a catalyst. The reaction only occurs between 400° and 900° C. The fact that metallic iron—especially if in a spongy or finely divided state—acts as a powerful catalyst in the dissociation of carbon monoxide (CO) into carbon and oxygen and of methane (CH_4) into carbon and hydrogen has long been known to metallurgists, but it is only comparatively recently that it has been recognised that the same catalyst is the cause of the deposition of carbon in firebricks during use.

Many experiments are not conclusive, but Bradshaw and Emery have found that the deposit is graphitic in character, and that it is produced whenever fireclay bricks are heated under reducing conditions in the presence of carbon monoxide. The film so formed is exceptionally hard and refractory. The author found that calcined clay which is free from iron compounds has

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[1] *Journ. Amer. Cer. Soc.*, 1923, 6, 904.

little or no action on carbon monoxide. The reaction may be represented by the equations $CO=C+O$; $2CO=C+CO_2$, the free oxygen in the former combining with the iron or iron compound.

The rate of reaction varies with the temperature and the catalyst, ferrous oxide being the most active at 500° C. and metallic iron between 800° and 1000° C. Above 850° C. the re-formation of carbon monoxide tends to occur.

The reaction can occur in the absence of iron compounds, but does not usually do so, *e.g.* the liberation of free carbon is increased by the presence of a little free magnesia. It is inhibited by reducing the proportion of free alumina and increasing the silica, and can be reversed (the carbon being oxidised) by supplying air and heating to at least 850° C.

The prevention of the deposition of carbon by adding copper or a copper compound (in solution or in the form of bronze powder) to the clay or by soaking the bricks in a solution of ammoniacal copper sulphate was patented in 1929 (Eng. Pat. 330,561). The similar use of organic boric acid salts or lead, nickel, manganese, mercury, zinc or cadmium in the form of metal or oxide was patented in 1931 (Eng. Pat. 404,699).

A brick to resist carbon monoxide must be very low in iron compounds, or it must have been fired at a temperature high enough to allow the iron to combine with the silica in the brick, and so prevent it from being reduced to the ferric or metallic state.

The carbon may occasionally effect the rupture of some of the pores of the brick or even cause it to break up completely. Sometimes the carbon forms a well-defined layer in the bricks, with a layer of unattacked clay both above and below it. The cause of this formation is not known, though F. Schreiber has suggested that it is due to hydrocarbon gases being enmeshed in the pores of the brick and then decomposed by the heat.

Blasberg has found that less than ½ per cent. of carbon in a firebrick is sometimes sufficient to loosen its texture and facilitate its disintegration.

The action of *superficially* deposited carbon is seldom detrimental and it is often advantageous, as it fills up small cracks in retorts, etc., and so enables them to be used for a much longer time than would otherwise be the case. It has even been suggested that the deposited carbon may increase the refractoriness of the goods. If the deposit is so thick as to be a serious hindrance to the heating of the retort (carbon being a bad conductor of heat) it may be scraped off periodically, or the retorts may be made very smooth inside by the manufacturer. In some cases, they are even covered with a thin layer of glaze, the claim being made that this facilitates the drawing and heating. Whatever action such glaze may have must be very small, and the repeated heating and cooling of the retort will soon make it break up, so that its value soon diminishes. It is, therefore, questionable whether it is worth the extra expense, even though this is not great.

The *strength* or *resistance to crushing* shown by firebricks *when cold* depends on the amount of fused material which cements the particles together, and is, therefore, related to the temperature attained in the kiln and to the duration of heating at this temperature. Fireclay bricks differ greatly in respect of the force required to crush them when cold, but this must not be less than will provide amply for the safety of any structures likely to be built of firebricks. A common-sense standard is the minimum allowed for the building bricks used in large structures, namely, 150 tons per square foot; the Institution of Gas Engineers only requires 1800 lbs. per square inch (=115 tons per square foot) as a minimum crushing strength for firebricks sold in accordance with their specification.

The Stettin (Germany) firebricks have an average of 5600 lbs. per square inch, and some firebricks made with a very high resistance to crushing have a resistance of 11,360 lbs. per square inch.

The strength of *very hot* fireclay bricks is less than when they are cold, as the cementing material begins to fuse and allows the bricks to be deformed, so that what is known as the *hot strength* or *refractoriness-under-load* is very important; it has even been described as the most important single test which can be applied to any brick.

There does not appear to be any connection between the refractoriness of a firebrick heated without any pressure and the refractoriness when the same firebrick is heated under a load. The latter is chiefly affected by the physical nature of the material. Thus, a very finely-textured firebrick with a refractoriness of Cone 33, began to collapse under a load of 28 lbs. per square inch at 1370° C., whilst a much coarser brick with a refractoriness of Cone 34, began to soften under the same pressure at 1250° C.

M. Gary, of the Gross Lichterfelde Testing Station, in 1910 made some tests of the crushing strength of firebricks at 1000° C. In each case he found that the bricks at this temperature had a greater resistance to crushing than the same bricks when cold. On heating to a higher temperature, a further partial fusion occurs and the strength is diminished. V. Bodin has found that the crushing strength of fireclay and other bricks (Table LXI.) shows two points of reduced strength—one at about 800° C., and the other at or above 1200° C., at which temperature most refractory materials become plastic. Some bricks are much stronger at 1000° C. than at any other temperature!

TABLE LXI.—VARIATION OF CRUSHING STRENGTH WITH TEMPERATURE.

Substance Tested.	Crushing Load in Kg.-cm.				
	At 20° C.	At 800° C.	At 1000° C.	At 1300° C.	At 1500° C.
Fireclay bricks A . .	195	125	105	740	40
„ CL . .	950	555	575	360	65
„ P . .	1110	485	1755	115	20
Alumina bricks—					
Bauxite	395	270	715	55	20
Corundum . . .	790	530	615	310	30
Carborundum . . .	415	425	585	150	70
Silica bricks A . . .	277	..	..	..	116
„ B . . .	276	..	..	..	27
„ C . . .	244	..	..	..	53
„ D . . .	171	..	..	..	1
„ S . . .	180	90	80	60	40
„ V . . .	240	125	185	160	100
Fused quartz . . .	2550	1040	780	1670	100
Crude zirconia . . .	395	275	345	90	10
Magnesite bricks—					
Eubœa	260	265	230	110	5
Styria	450	295	190	115	30
Chromite bricks . . .	450	450	425	215	75

Fig. 85 shows a typical strength-temperature curve of fireclay bricks. The great reduction in crushing strength at about 800° C. is not generally known, but it should be taken into consideration in designing furnaces, etc.

Bleininger and Brown have found that, with a load of only 50 lbs. per square inch, at a temperature of 1350° C., all except the best fireclay bricks are sufficiently soft to be pressed out of shape, and they, therefore, suggested that no bricks should be regarded as of the highest grade which shrink more than 1 inch when tested in a vertical position under a load of 50 lbs. per square inch at a temperature of 1350° C. These investigators also concluded that there is some connection between the strength of firebricks under these conditions and their composition, inasmuch as no fireclay stood this test if it contained more base than is indicated by the formula $0{\cdot}225RO.Al_2O_3.2SiO_2$, and that if a more siliceous fireclay is tested in this manner it will collapse unless it contains a correspondingly lower proportion of base. Thus, with 4·4 molecules of silica per molecule of alumina, the bricks collapsed under a load of 50 lbs. per square inch at 1350° C. when bases equivalent to only 0·17RO were present.

Fireclay bricks collapse gradually, but silica bricks do so suddenly.

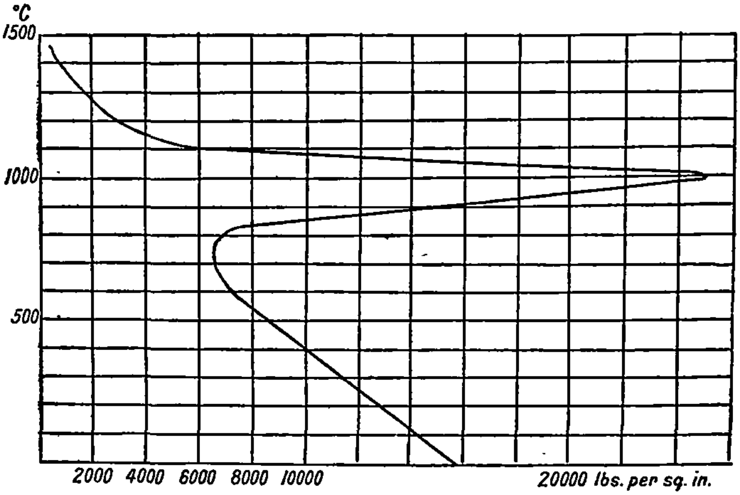

Fig. 85.—Strength of fireclay bricks (V. Bodin).

As firebricks are chiefly used at high temperatures, their crushing strength at the temperatures to which they are subjected in use is far more important than their strength when cold.

Under a very small load (1 kg. per sq. cm. or 14 lbs. per sq. in.), fireclay bricks begin to soften between 1100° C. and 1300° C., and rapid collapse occurs between 1370° C. and 1700° C. The range of temperature between the first observable softening and complete collapse is usually between 100° C. and 250° C., but with some fireclay bricks it is as much as 500° C.

Mellor has shown that the variation in the softening-points of a number of British fireclays when subjected to the loads is as indicated in Table LXII., which is taken from the 1914 *Report of the Refractories Committee of the Gas Engineers Institution*.[1]

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[1] The rate of heating was 10° C. per minute, to compare with the tests made without a load.

J. W. Mellor has suggested that the relationship between the bending temperature and the pressure applied may be represented by the equation—

$$\text{Bending temperature} = Ce^{-kW}$$

where C denotes the bending temperature (in cones) without a load; W represents the pressure in lbs. per square inch; e is the exponential constant; and k is a numerical constant dependent upon the particular clay employed, the mode of manufacture of the test-pieces, etc., and it ranges from 0·003 to about 0·02 in value.

TABLE LXII.—EFFECT OF PRESSURE ON REFRACTORINESS.

Group I.			
Experimental Number.	Normal Melting-Point.	Melting-Point under Pressure of 54 lbs. per Square Inch.	Melting-Point under Pressure of 72 lbs. per Square Inch.
	° C.	° C.	° C.
1	1650	1435	1380
2	1630	1410	1350
7	1580	1380	1350
12	1690	1435	1410

Group II.			
Experimental Number.	Normal Melting-Point.	Melting-Point under Pressure of 84 lbs. per Square Inch.	Melting-Point under Pressure of 112 lbs. per Square Inch.
	° C.	° C.	° C.
3	1690	1460	1380
4	1710	1500	1435
5	1670	1460	1380
9	1750	1580	1580
10	1690	1500	1460
1	1670	1460	1380
16	1730	1460	1410
17	1770	1520	1410

N.B.—No. 17 is a typical china clay of first-class quality, and was used for the purpose of comparison. It is interesting to note that some of the clays very nearly equal it in refractoriness.

The softening of bricks under pressure or load is due to small quantities of fluxes in the clay which are not sufficiently large to cause actual fusion, but are large enough to bring about a slightly viscous condition which allows the brick to yield gradually. It will usually show up more quickly in a brick whose constituents have been finely ground and closely pressed together than in a coarse, loose-textured one. The application of pressure to a hot brick brings the particles more closely together, makes any molten material present still more mobile, and so appears to lower the refractoriness. A further result of the particles being brought closer together when under pressure is that the chemical changes which occur within the brick take place at a more rapid rate.

The presence of too large a proportion of fluxes simultaneously with a pressure on the hot bricks is one of the primary causes of the premature failure of some fireclay bricks, but this is not the only cause for the great weakening which occurs at about 1300° C., regardless of the amount of fluxing materials present; even an almost pure china clay gives the same result.

Fig. 86, due to K. Endell, shows the effect of a small pressure on fireclay and other refractory bricks at high temperatures.

The influence of various substances on the strength of firebricks under load has been carefully investigated by E. Sieurin and F. Carlsson, who prepared mixtures of one part of chamotte (all of which was finer than 7-mesh) burned at Cone 14 (1410° C.) and one part of raw clay, and the mixture was varied by the addition of various proportions of silica, alumina, iron oxide, lime, and magnesia to the raw mixed materials. These various mixtures were made into cubes, fired at Cone 14, and then cut to exactly 30 mm. square. These were heated in an electric furnace under a pressure of 28 lbs. per square inch (2 kg. per sq. cm.), and the softening-point taken as the temperature at which a contraction of 0·3 per cent. of the original length occurred after the test-pieces had been exposed for two hours to the standard load.

Figs. 87 to 91 show the effect of the various additions upon the softening-points under pressure (I) and the normal fusing-points (II) of a fireclay investigated by Sieurin and Carlsson. The remarkable differences in the shapes of the two sets of curves should be noted. It will also be observed that—

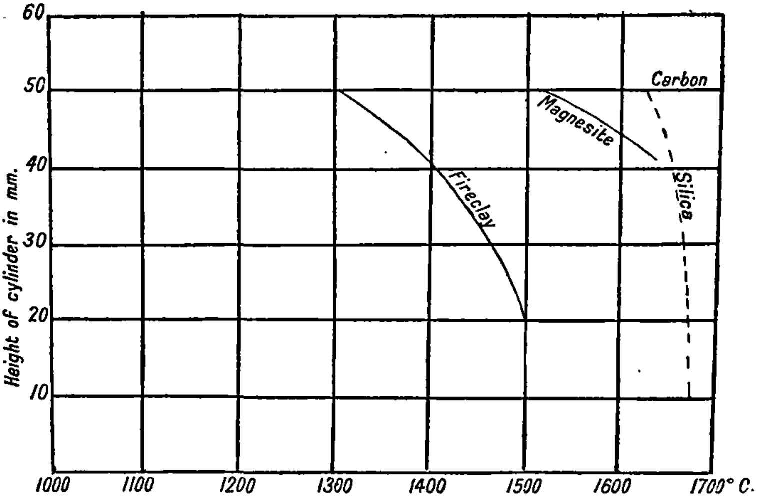

FIG. 86.—Crushing of refractory bricks at high temperatures under a load of 1 kg.-cm.[2] (K. Endell).

Silica.—The minimum softening temperature obtained is when between 60 and 70 per cent. of silica is present.

Alumina increases the softening-point until about 70 per cent. of alumina is present; with 68 to 80 per cent. of alumina the softening-point suddenly falls and then very slowly rises with still higher percentages.

Iron oxide, up to about 6 per cent., rapidly lowers the softening-point of the clay. With 6 to 12 per cent. the softening-point is only slightly affected, but with less than 6 or more than 12 per cent. it falls rapidly.

Lime, up to about 1 per cent., causes a rapid fall in the softening-point of the clay. With more than 1 per cent. the softening-point continues to fall, but at a less rapid rate.

Magnesia, up to about 0·25 per cent., causes a rapid fall in the softening-point; with larger proportions the rate of fall is less rapid.

In short, these investigations show that even small proportions of fluxes reduce the resisting power of refractory materials to pressure at high temperatures.

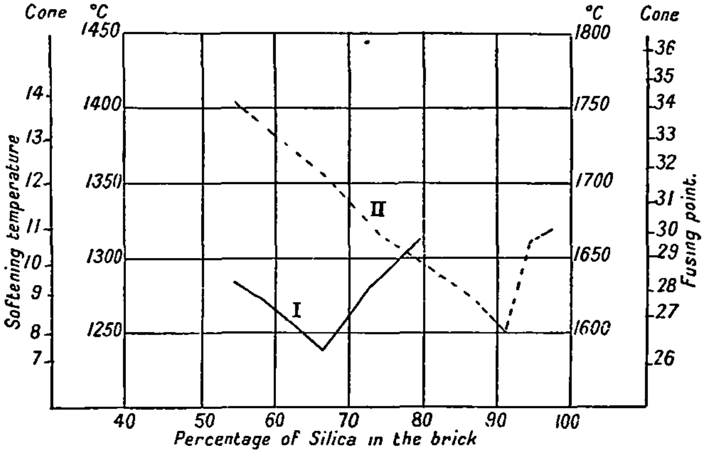

Fig. 87.—Effect of silica on fireclay bricks.

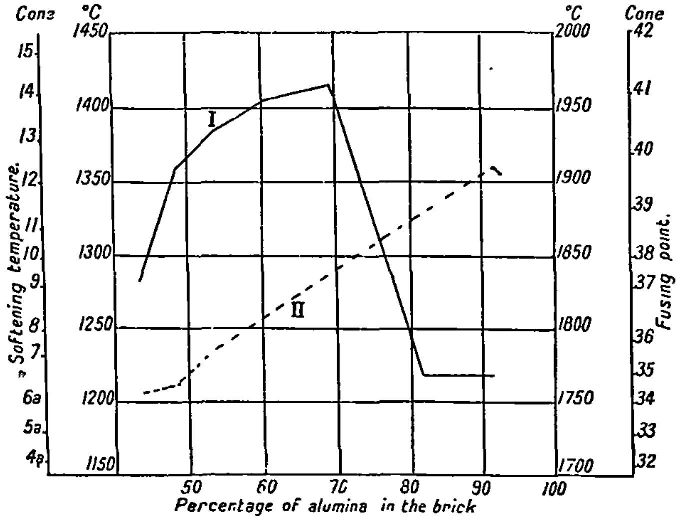

Fig. 88.—Effect of alumina on fireclay bricks.

The relation of porosity and volume changes to the strength of hot firebricks is rather interesting. G. A. Loomis has pointed out that—

(1) Bricks which are capable of withstanding a pressure of 40 lbs. per

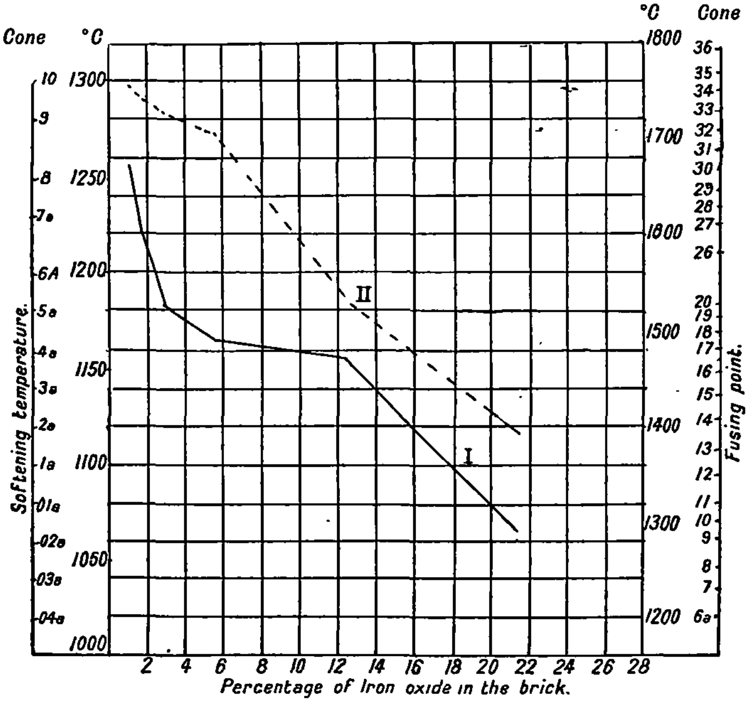

FIG. 89.—Effect of iron oxide on fireclay bricks.

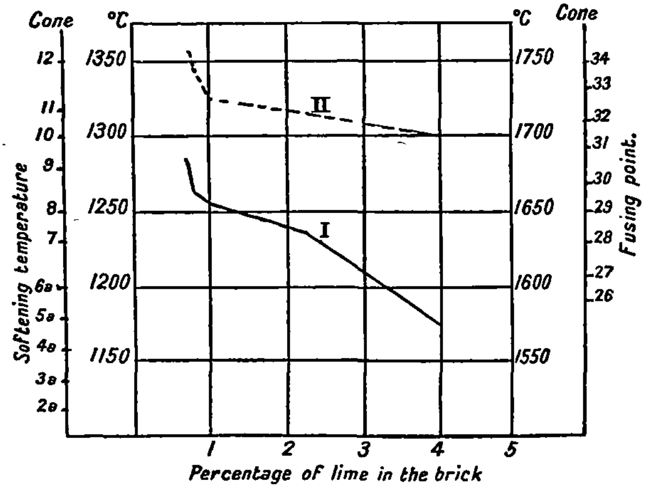

FIG. 90.—Effect of lime on fireclay bricks.

square inch at 1350° C. generally show only slight changes in volume and in porosity when re-heated to temperatures up to 1425° C.

(2) Bricks which show distinct overburning, by pronounced expansion at temperatures below 1400° C., invariably fail in the load test.

(3) The changes in volume and in porosity of the bricks burned at some temperature between 1350° C. and 1425° C. serve, in a measure, as a criterion of their ability to pass the load test.

(4) Most of the bricks which show a porosity-decrease not exceeding 5 per cent. and a volume-change not exceeding 3 per cent. (about 1 per cent. in linear dimensions), when burned at 1400° C., will pass the load test.

(5) Bricks which show a decrease in porosity exceeding 5 per cent. or an expansion or contraction in excess of 3 per cent. by volume (1 per cent. in length) at 1400° C. usually fail to pass the load test.

(6) The use of limiting porosity and volume changes for clay firebricks burned at 1400° C. would serve as a means of eliminating from consideration a large number of bricks which fail in the load tests.

(7) Bricks which fail in the load test—due to the failure of the bond—may show marked changes in volume or porosity in burning, and often show very low cold-crushing strengths.[1]

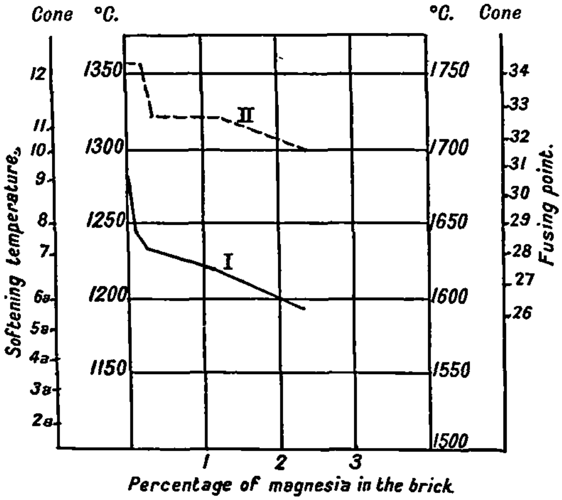

FIG. 91.—Effect of magnesia on fireclay bricks.

(8) No definite relationship seems to exist between the softening-point of a firebrick and its ability to withstand load at high temperatures. However, all bricks which softened below Cone 28, whether siliceous in character or not, failed completely in the load test. It seems advisable, then, to specify Cone 28 as the minimum softening-point for any clay firebrick. It is probable that bricks containing less than 65 per cent. of silica should have a minimum softening-point of Cone 31.

Bricks having a low refractoriness-under-load can sometimes be greatly improved by prolonged heating at a higher temperature during the burning.

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[1] For further information on the effect of fluxes on the refractoriness under pressure see *Trans. Cer. Soc.*, 1938, **37**, 168.

In this treatment, the glassy material in the bricks will tend to dissolve more of the aggregate and so produce a glass of much higher melting-point. As a result, when the refractoriness-under-load test is applied a higher result will be obtained.

Many bricks which give a low result when the refractoriness-under-load is determined behave satisfactorily in use, because in the latter case only the face of the brick attains a high temperature.

The *relation of composition to refractoriness-under-load* is shown in fig. 86. In the case of fireclay bricks, the more siliceous the clay the less is the difference between the refractoriness with and without a load. The gradual loss of shape which fireclay bricks undergo, compared with the sudden loss of silica bricks, is also noteworthy.

The *refractoriness-under-load* (p. 356) may be determined in several ways, of which the most important are:

(i) The pressure or load is kept constant and the temperature is raised gradually until the test-piece loses its shape completely.

(ii) The pressure is kept constant, the temperature is raised gradually, and the height of the test-piece is measured at regular intervals. A graph is drawn showing the change of shape with the change in temperature (see fig. 86); this is the most popular form of the test. The temperature at which the height of the test-piece first shows a reduction is often termed the t_o-point; that at which it is reduced by 3 mm.[1] (a wholly arbitrary figure) is known as the t_a-point, and the temperature at which complete collapse occurs as the t_e-point.

(iii) The temperature may be maintained constant at a specified value and the pressure gradually increased until deformation occurs.

(iv) Both the temperature and pressure may be kept constant and the time taken to produce a pre-arranged amount of deformation (10 per cent.) may be noted, or the height of the test-piece may be noted at regular time-intervals and a graph plotted. This form of the test is specially useful when investigating the effect of prolonged heating on refractory materials.

The " load " may be varied to suit the user's requirements, but 50 lb. per sq. in. and 1 kg. per sq. cm. are the most popular.

When the second method is used, it will be found that fireclay bricks collapse slowly as the temperature increases above 1300°–1350° C., but carbon, silica, and carborundum bricks collapse very suddenly; magnesite bricks collapse more quickly than fireclay bricks, but more slowly than silica bricks.

It is important that a correction should be made for any expansion of the supports and thrust blocks during the test, as otherwise the results may be 100°–250° C. too high.[2]

Transverse tests are increasingly preferred to compression or crushing tests, as they are easy to make and require no costly machine. The brick, or other test-piece (a bar being preferred to any other shape), is placed on two steel knife edges as far as possible apart, and a gradually increasing weight is applied through a third knife edge resting on the top of the test-piece half-way between the two others. To prevent the sample being cut by the upper knife, the latter may rest on a sheet of glass. The load is increased until fracture occurs, the results being reported by means of the formula: $E=\frac{kpl}{bd^2}$

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[1] Clews and Green (*Inst. Gas Eng.*, *25th Rep. Refract. Matls. Comm.*, 1934, pp. 8–29) have suggested that a reduction of one-tenth of the height of the test-piece should be taken as the t_a-value, as with this amount of deformation no cracks usually occur.

[2] Clews, Green and Green, *Trans. Cer. Soc.*, Preprint, Nov. 1936.

where E denotes the breaking strain in lbs. per square inch ; k is a constant depending on the material ; b is the breadth ; d the depth ; and l the length between the two supports, all of these dimensions being in inches; and p is the breaking load in lbs. ; for fireclay bricks k is 1·5.

The *tensile strength* of refractory materials is deserving of more consideration than it has received, because, in some cases, the failure of refractory materials has been due to the tension rather than the pressure on them. Scarcely any results of such investigations have been published, and if more information were available it would be of great value.

The strength of fireclay bricks may be increased or diminished by careful adjustment of the proportions of the various materials used. Fusible materials will increase the strength of the cold bricks, and refractory substances will increase the strength of the hot bricks. Hence, careful consideration is necessary in order to produce bricks of a given strength.

Rapid tensile tests give different results from those obtained by heating fireclay goods for a very long time at a given temperature under a definite tension. In most cases they retain their shape well, except for a slight extension, but eventually they fail suddenly—probably as the result of a gradual increase in the amount of glassy matrix. Siliceous clays are more durable under prolonged heating under tension than are highly aluminous clays. The presence of grog reduces the resistance to prolonged tension.[1]

At 1500° C. or below most fireclay goods will fail under a tension of 10 lb. per sq. in. The extension begins at a much lower temperature, but increases very rapidly as the temperature of failure is approached. There is usually a contraction at 1350°–1450° C., and shortly after this a rapid increase in expansion resulting in failure. Unfortunately, the contraction-point is not definite enough to be regarded as a critical point.[2]

The *modulus of elasticity* (Young's modulus) is increasingly regarded as an important physical property. It is determined by measuring the maximum tensile load which can be applied so as to stretch the material without producing a permanent increase in length after the load has been removed. With fireclay bricks it is usually $2–5 \times 10^6$ lb. per sq. in.; it is lowest with underfired bricks. It increases with an increase in the silica-content of the bricks. Most refractory materials lose their elasticity at 800°–1000° C. and become plastic. The ratio obtained by dividing the modulus of elasticity by the crushing strength appears to be an important factor. Heindl and Prendergast[3] have found that with most fireclay bricks and silica bricks Young's modulus of elasticity increases with the temperature up to 600° C., and that there is a linear relation between this and the percentage of silica.

The effect of *torsion* on fireclay bricks has been investigated by Roberts and Cobb[4] and others. The modulus of torsion is reduced at 800°–1000° C., and this change is accompanied by a lesser tendency to spall at higher temperatures. With highly siliceous mixtures the modulus of torsion increases with the temperature.

The modulus of torsion is important as it indicates the amount of stress induced by the differential expansion resulting from the temperature gradient, and this, in turn, affects the spalling.

According to Roberts and Cobb[5] grog produces bricks which are more

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[1] See Partridge and Adams, *J. Soc. Glass Tech.*, 1931, **15**, 190–203.

[2] Partridge and Adams, *J. Soc. Glass Tech.*, 1931, **15**, 190.

[3] *J. Res. Nat. Bur. Stand.*, 1934, **13**, 851.

[4] *Trans. Cer. Soc.*, 1933, **32**, 22; 1936, **35**, 182; 1938, **37**, 296.

[5] *Trans. Cer. Soc.*, 1936, **35**, 203.

resistant to torsion than those made with silica, but the strength depends greatly on the treatment in the kiln.

Torsion tests made at various temperatures showed that, up to about 800° C., both the ultimate shear strength and the rigidity modulus of fireclay bricks remain fairly constant, but above this temperature the shear strength increases and the rigidity modulus diminishes. In mixtures of clay and quartz, the same properties increase steadily up to 800° C., but above this temperature both decrease. The authors claim that an increase in the ratio shear strength/rigidity modulus with an increase in temperature indicates the development of an increased resistance to spalling. The changes in the ratio remain small until pyroplasticity [1] is developed.

The *brittleness* of fireclay and grog bricks after repeated heating appears (according to Mellor and Austin) to be due to—

(1) A reduction of mechanical strength due to the volatilisation of alkalies and silica.

(2) Local shrinkage and strain due to irregular patches of crystals formed by the chemical reactions which occur when the material is heated.

(3) Crystallisation, which may to some extent be prevented by a rapid cooling to 800° C., or a little lower, though not all firebricks made exclusively of clays can withstand this treatment.

Resistance to abrasion is often important in deciding the relative value of various firebricks for a given purpose. Thus, for furnaces, the action of the poker during stoking must be considered. In roasting furnaces, blast furnaces, gas retorts, and coke ovens, the charging, movement, and removal of the material will tend to wear away the refractory work.

High resistance to abrasion is best secured by means of a close, hard, and well-burned surface on the bricks; a more porous interior may be provided if desired, though it is advantageous, where other conditions do not prevent it, to have the bricks dense throughout.

When bricks are made of grog and binding clay, the greatest resistance to abrasion is secured by the use of a bond-clay which vitrifies readily (Seger Cone 3) without the bricks losing their shape below Cone 26, and shrinking unduly. The material in the moulds should be rammed or tamped thoroughly so as to ensure the particles being as close together as possible.

A useful abrasion test suggested by Hartmann and Kobler consists in cutting a groove in the ends of the brick so as to expose the maximum area to cutting and then applying the brick at a constant pressure of 25 lbs. for five minutes to a carborundum grinding wheel of grit 16, grade 1, 12 inches diameter and 2 inches across the face, revolving at a speed of 1560 feet per minute. The depth of the groove is measured before and after the test, the difference being proportional to the resistance of the brick to abrasion. Under this test, the groove is lengthened 0·05 to 0·25 inches in five minutes in the cold, and rather less when the bricks are hot. Firebricks are often more resistant to abrasion when heated to any temperature well below the sintering-point. At higher temperatures, the resistance to abrasion is reduced as the fluid bond makes the bricks weaker.

The *fusibility* and *refractoriness* of fireclay bricks is usually that of the clay of which they are made, but owing to a partial volatilisation of the alkalies and silica in the clay, the bricks may be rather more refractory than the raw clay. Many of the statements on the heat-resistance of clays which have been published are misleading, as they do not indicate the conditions under which the refractoriness was determined.

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[1] Pyroplasticity is plasticity at a high temperature; it is different in its origin and in many other respects from plasticity due to the presence of water.

Fireclays—like all mixtures of silica and alumina—when heated and cooled produce only one crystalline product, mullite, and a molten glass which eventually solidifies. There is no eutectic of silica and alumina, but one of silica and mullite which melts at 1545° C., contains 5·5 per cent. of alumina and 94·5 per cent. of silica, and consists of 7·7 per cent. of mullite and 92·3 per cent. of silica. Therefore, all *perfectly pure* refractory materials consisting of alumina and silica *begin* to melt at 1545° C., as this is the melting-point of the eutectic.

The larger the proportion of glass (eutectic), especially if it is increased by the presence of fused impurities, the shorter will be the time of heating (or the lower will be the temperature) at which signs of fusion become visible. In other words, the softening, sintering, and eventual fusion of fireclay bricks may be regarded as due to (*a*) the gradual melting of the more readily fusible constituents, (*b*) the solution of other substances in the molten material, and (*c*) the formation of chemical compounds which are more fusible than the substances from which they are formed. This last is usually attributed to *fluxes*, *i.e.* substances which combine with others to produce a molten mass.

If a firebrick contains only a small proportion of alkali, lime, or iron fluxes, these will soon combine with so much clay and silica that they become saturated and then form a solution which is practically infusible at the temperature attained. If the brick contains a larger proportion of fluxes the molten glass will take longer to become saturated, and the amount of clay and silica dissolved and the amount of molten material produced will be correspondingly greater; it may be so large as to cause the obvious destruction of the bricks. If a brick is raised to a higher temperature, the fluxes and molten material will again become active, and more clay and silica will be dissolved in the molten material, until saturation at the higher temperature is reached. The residual material—if the bricks have been sufficiently well burned—will probably consist largely of felted crystals of mullite (p. 147) with, possibly, some free silica in the form of cristobalite. The strength of fireclay bricks at high temperatures is largely due to this mass of felted crystals embedded in a glassy matrix.

The mixture of clay and free silica having the lowest refractoriness corresponds to about 40 per cent. of true clay and 60 per cent. of free silica. On the other hand, the maximum amount of mullite which can be formed from fireclay (without any addition of alumina) is about 56 per cent. (*i.e.* in a brick containing 40 per cent. of alumina). To produce bricks with a larger percentage of mullite it is necessary to add almost an equal weight of alumina —preferably in the form of calcined bauxite or diaspore.

The chief advantages of a larger proportion of mullite in a brick are (i) an increased refractoriness, (ii) a greater refractoriness-under-load, and (iii) a greater resistance to corrosion.

The fused material tends to draw the other particles together, so that the mass, as a whole, shrinks. This contraction continues until the molten material is too viscous to draw any more particles together. The mass has then attained its maximum mechanical strength, and a further heating to a higher temperature, or even a prolonged heating at the same temperature, will cause a reduction in strength. A considerable amount of fusion can occur without any noticeable loss of shape provided no pressure is applied, but a very small pressure may suffice to squeeze some of the molten material from the hot brick. Hence, the refractoriness of fireclay bricks depends principally on the glassy matter present, as this is chemically much more active and melts at a much lower temperature than the crystalline constituents.

It may be taken as a general rule that no firebricks made exclusively of British fireclays have a greater refractoriness than corresponds to Seger Cone 34 (1750° C.), that most of the better ones correspond to Cones 31 and 32, and that a considerable number will not stand a more severe test than Cone 29. It will be remembered that Cone 26 is generally regarded as the minimum for a refractory material.

The remarks previously made with reference to the refractoriness of clays apply with equal force to fireclay bricks. The fact that a fireclay brick does not soften or lose its shape when heated slowly in a clean atmosphere to a temperature of 1700° C. is no criterion of its resistance under industrial conditions. On the contrary, a brick with a dense surface or a close texture will often prove much more durable than a porous brick with a higher fusing-point. Bleininger and Brown have concluded from their investigations that a much better test is the amount of deformation which a firebrick undergoes when heated under a load as described on p. 356.

The effect of prolonged or repeated heating on fireclay bricks depends on the temperature and the total duration of the heating. If the temperature is sufficiently high to increase the proportion of vitrified or fused matter, any increase in either the temperature or the duration of heating will increase the amount of vitrification. This may result in the strength of the hot bricks being so reduced that they collapse under the pressure of superincumbent material. Sometimes no appreciable diminution in strength is observed, but the bricks are found on examination to contain an increased proportion of crystalline matter, not readily soluble in hydrofluoric acid, and generally regarded as mullite though formerly it was mistaken for sillimanite.

The harder a fireclay brick is fired the larger will be the amount of mullite formed, the stronger will be the brick and the smaller its expansion when in use. For further information on the formation of mullite see p. 147.

Fireclay bricks differ from those made of silica in the rate at which they collapse on prolonged heating at their softening temperature. Silica bricks, being composed almost entirely of a single substance (silica), collapse somewhat suddenly when the softening-point is reached or passed, but fireclay bricks are more complex in structure and collapse much more slowly. This is an important characteristic which is of great value in some industrial processes, as the gradual collapse acts as a warning.

When a fireclay brick (or grog) is heated repeatedly at a temperature above 1200° C., a considerable proportion of the alkaline matter and some of the silica are gradually volatilised. The brick thus becomes more refractory, but the loss of cementing material (of which the alkalies form a part) also reduces the strength of the brick. In many situations where firebricks are used (as in blast furnaces, cupolas, coke ovens, etc.), the precise opposite occurs, and the bricks become richer in alkalies—derived from the material with which they come in contact—and, therefore, become more fusible. In works where coal is washed before it enters the ovens, the salt absorbed by the coal from the washing water often has a serious effect on the refractoriness of the bricks of which the oven is built.

The most readily volatile impurities are the alkalies (soda, potash, and lithia). Iron in the form of ferric chloride is readily volatile. Lime, silica, and some alumina may be volatilised by being reduced to their elements and again becoming oxidised on being slightly cooled. Attempts have been made to purify fireclays by heating them with hydrochloric acid or with ammonium chloride, so as to form volatile chlorides, but with small success.

On repeated or prolonged heating at a temperature of 1450°–1550° C. most fireclay bricks shrink[1] considerably. This shrinkage diminishes with each time of heating, but never entirely ceases, though if a fireclay brick is, in course of manufacture, heated for several hours at a much higher temperature than any it is likely to reach when in use, the subsequent shrinkage will be negligible. If, on the contrary, the brick has been insufficiently heated before use, it may shrink so much as to cause serious damage. The linear measurement of shrinkage, though customary, is not strictly accurate, as shrinkage does not usually occur uniformly in all directions. Hence, the contraction in volume should be determined in all accurate work. For most purposes the linear shrinkage is sufficiently accurate.

Bricks which shrink appreciably in use are quite unsuitable for some purposes, of which by-product coke ovens, arches and crowns of furnaces and kilns, form notable examples. It is this fact which has led to such an extensive use of silica in place of fireclay in lining certain furnaces, and to unfair and incomplete comparisons of British and foreign firebricks.

Change of volume on heating is the result, primarily, of insufficient burning during the manufacture of the goods. If the firebricks are made of clay and fired at Seger Cone 5*a* or 6*a*, and are afterwards used at Seger Cone 11, it is not surprising that they should shrink still further. If they had been heated to the temperature corresponding to Cone 14 in course of manufacture, the further shrinkage would have been inappreciable.[2] To overcome the drawbacks due to shrinkage, either the users of the firebricks must allow for the shrinkage as far as it is possible to do so, or they may insist on the bricks being burned at a higher temperature.

In his own interests, as well as in those of his customers, the manufacturer should see that firebricks are burned at such a temperature, or that the heating in the kiln is continued for so long a time, that the expansibility or shrinkage at the temperatures at which the bricks are to be used can no longer exert any detrimental influence. This usually means a finishing temperature corresponding to Seger Cone 12 (1350° C.) or above.

The repeated heating of fireclay bricks is also accompanied by numerous other obscure yet important phenomena. Thus, the loss of alkalies which occurs is one reason why grog is preferable to raw clay in the manufacture of refractory goods. Having been heated intensely before use and again when made up into articles, it loses sufficient alkali in the double heating to produce a superior product. Mellor has found that a piece of Staffordshire saggermarl, heated seven times to nearly 1200° C., lost nearly 22 per cent. of the total alkalies present; and the author has ascertained that a slightly larger loss occurred on heating some Newcastle fireclay bricks three times to the bending temperature of Seger Cone 9 for twelve hours at a time.

The maximum safe working temperature for fireclay bricks seldom exceeds 1545° C., and is much lower with some bricks. Much depends on the duration of the heating at high temperatures and the proportion of the brick which reaches these temperatures. The safe working temperature is greater in bricks which have been fired at a higher temperature than that at which they are to be used. The best results are obtained with bricks which have been subjected to prolonged heating at a temperature only a few degrees below that at which they fail in the refractoriness-under-load test. The reason is that

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[1] Some fireclay bricks swell when heated; this is due to the formation of gas and partial fusion of the impurities in the clay. This swelling can only occur in inferior bricks or in those which have absorbed a considerable amount of slag, etc., whilst in use.

[2] A momentary heating at the higher temperature is not sufficient; the heating must be prolonged to effect the proper shrinkage of the material.

this prolonged heating causes the solution of more silica and alumina in the glassy matrix and so raises its melting-point.

The *susceptibility* of fireclay bricks to sudden changes in temperature is important. Many, though not all, fireclay bricks disintegrate if they are cooled too rapidly, and great care is, therefore, necessary, though fireclay bricks are not nearly so sensitive as those made of silica. Dense firebricks usually suffer most from rapid cooling, and, consequently, many manufacturers add (i) grog (see Grog Bricks, p. 379), (ii) kieselguhr, or (iii) sawdust or other combustible materials to the clay so as to increase its porosity in the kiln.

It is commonly regarded as a valuable property of Glenboig bricks that they may, whilst at a bright red heat, be dropped into water without being damaged. This indicates their indifference to sudden changes in temperature, but as a test it is unnecessarily severe.

It is generally supposed, and with a considerable measure of truth, that bricks composed of finely ground clays are more liable to split or spall when heated and cooled than bricks which are coarse-textured. When a finely ground brick gives way under sudden changes of temperature, it does so along one or more well-marked lines, and, as a result, pieces often come off bodily, and the brick is said to *spall.*

The resistance of firebricks to spalling may be tested by heating carefully weighed bricks to a temperature of 1350° C., maintaining them at that temperature for one hour to ensure a uniform temperature throughout, and then exposing them to a blast of cold air from a ¾-inch nozzle delivering 27 cubic feet of air per minute for a period of 15 minutes. This test is repeated about ten times, after which the sample is re-weighed. A very good grade of firebrick of open texture should show less than 12 per cent. loss of weight by spalling, whilst close-textured bricks may show up to 65 per cent. loss. In this respect, fireclay bricks are much stronger than silica and magnesia bricks, which are completely destroyed with less than ten heatings. If the firebricks contain up to 40 per cent. of grog, their resistance to spalling when quenched in water appears to be roughly proportional to the percentage of grog present, though this statement does not necessarily apply to all fireclay bricks.

In coarse-textured bricks, owing to their structure, the strain is relieved by a great number of small fissures between the coarse, hard grains, which are not sufficiently continuous to permit the mass falling to pieces. *The shattering of firebricks* may be regarded as being caused by the particles of the brick being too tightly packed to move freely when suddenly heated or cooled, and, consequently, any arrangement which will make them move more freely in response to a sudden change of temperature will increase the durability of the brick. This extra freedom of movement may be conferred by leaving sufficient space between the particles, but the full amount of space needed cannot be supplied without serious reduction of strength when a firebrick is composed of such fine and small particles as are found in most clays. An alternative method would be to substitute for the spaces a soft material which would yield under pressure, but this is not easy to procure. The firebrick manufacturer must, therefore, effect a compromise by providing as many spaces as possible between the particles, and he does this by employing a material composed of larger particles than unfired fireclay, and of similar refractoriness, viz. grog.

In fireclay bricks the chief tendency to spall occurs at temperatures below 800° C., and is chiefly due to any free silica present. Numerous suggestions have been made as to the cause of spalling, but none is wholly satisfactory. It has been attributed to:

(*a*) irregular expansion on heating;

(*b*) shearing stresses resulting from expansion and contraction;

(*c*) forces measured by the modulus of torsion and other allied factors;

(*d*) a difference in temperature (*temperature-gradient*) in various parts of the brick due to uneven heating or cooling;

(*e*) compression (due to expansion) sufficiently great to cause shearing (this is chiefly due to bad furnace design);

(*f*) differences in the coefficient of expansion of the surface-layer and that of the body of the brick, which are large enough to shear off the surface-layer (this is chiefly due to the penetration of slag or to some structural change, occurring during the use of the bricks, which only penetrates to a small depth below the surface);

(*g*) the presence of several constituents having widely differing rates of expansion or contraction;

(*h*) large changes in crystalline structure, particularly if they occur rapidly;

(*i*) weak mechanical structure, however caused;

(*k*) low diffusivity, creating differences in the temperature of different parts of the same brick, whereby stresses are set up in the bricks;

(*l*) instability of the glassy matrix at high temperatures; and

(*m*) great rigidity of structure, preventing the relief of strains set up by changes in temperature, which, however, are relieved if the temperature is raised slowly.

Tests[1] made by passing polarised light through a brick made of transparent bakelite and viewing the isochromatic bands formed when the transmitted light was passed through an analyser showed that:

(i) the lines in the isochromatic bands are also lines of principal shear;

(ii) the stresses set up by rapid heating of the surface are usually low at the corners and in the interior and reach their highest value along the heated surface at a distance from the corners;

(iii) the maximum shearing stresses are equal to half the maximum resultant stresses;

(iv) no high tensile stresses are produced by rapid heating, but they can develop on sudden cooling;

(v) shear cracks tend to enter at 45° to the surface, but are sometimes parallel to it, tension cracks enter and leave at 90° to the surface and follow (broadly) the lines of principal stress;

(vi) when a crack has started the stress-distribution is much altered;[2]

(vii) the strain is proportional to the size, coefficient of expansion, and temperature-gradient;

(viii) the tendency to spall is $S=k\frac{\epsilon}{\delta\phi}$, where S=tendency to spall, ϵ= coefficient of expansion, δ=diffusivity, ϕ=maximum shearing strain; if N is the number of heatings and quenchings endured without cracking, the points corresponding to N as ordinates and S as abscissæ lie on a smooth rectangular hyperbola (Booze[3] and Phelps[4] independently reached similar conclusions to Norton, but found that the diffusivity had no appreciable effect);

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[1] F. H. Norton, *Refractories*, 1931, New York.

[2] E. W. Preston, *J. Amer. Cer. Soc.*, 1926, **9**, 654.

[3] M. C. Booze, *Proc. Amer. Soc. Test. Matls.*, 1926, **26**, 277–280.

[4] S. M. Phelps, *Amer. Refract. Inst.*, Tech. Paper 1, 1926.

(ix) the resistance to spalling was at a maximum in bricks containing 40–50 per cent. of binder and 50–60 per cent. of grog, *i.e.* the proportion of binder needed to fill the interstices and coat the particles of grog thinly; both above and below this proportion the resistance to spalling diminishes;[1]

(x) the resistance to spalling increases with the coarseness of the grog for grog in a series of sizes between 2-mesh and 20-mesh inclusive;[1]

(xi) the resistance to spalling increases (roughly) with the temperature at which the bricks are burned.

Unfortunately, spalling is most frequent among dense, fine-grained, hard-burned bricks, and the steps taken to reduce spalling—increasing the porosity—inevitably reduce the resistance of the bricks to compression, abrasion, and corrosion. In so far as spalling is affected by the method of manufacture, bricks made by the semi-dry process spall least, those made by the wire-cut process next, and those made by hand-moulding spall most.[2]

Spalling is less with flexible bricks than with rigid ones, unless the bricks are too tightly held in place.

J. F. Hyslop[3] has found that resistance to spalling is due to both the tensile and shear properties of the bricks, and that a high resistance to one type of stress does not necessarily indicate a high resistance to the other. He states that an ideal body for resisting thermal shock has a high resistance to both normal and tangential stresses.

One of the chief difficulties in the study of spalling is that almost every property which appears to cause it is possessed by some material which does not spall. Thus the presence of glassy material is usually a cause of spalling, but vitreous silica (p. 704), which is wholly glassy, does not spall. Similarly, a high coefficient of conductivity is often a cause of spalling, but fused alumina and carbides, which are highly conducting, do not spall. Before all the causes of spalling can be understood, much more will have to be known about the elasticity and plasticity of refractory materials over a long range of temperature and under various conditions of heating. A more exact form of " spalling test " is also required, those now in use being too crude.

Resistance to spalling is best ensured (*a*) by using a coarse grog with little " fines," (*b*) by having a sufficient porosity, and (*c*) a low coefficient of expansion. Among preventible causes of spalling are (*a*) too low a proportion of bond, (*b*) insufficient tempering or mixing, (*c*) irregular pressing during shaping, and (*d*) irregular heating and cooling in the kiln.

Fireclay bricks tend to spall much less readily than most silica and magnesite bricks. This is usually attributed to the material forming the walls of the pores cracking and so relieving the strain caused by thermal shock, which would, with denser materials, result in spalling. This is not, however, the only cause.

The tendency of fine-grained bricks to fall to pieces has been considerably overrated, and many bricks which ought, according to their density and fine texture, to spall, prove very durable when in use. In any case, the remedy for this defect consists in properly grading the sizes of grains of the material before making it into bricks, just as the material is graded in the manufacture of concrete.

The *specific heat* of fireclay bricks is very low (about 0·25). It rises rapidly as the temperature increases. The following figures were obtained by S. T. Wilson and A. D. Holdcroft:—

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[1] Norton, *Amer. Refract. Inst.*, Tech. Paper 1, 1926.

[2] This is confirmed by Bennie, *Trans. Cer. Soc.*, 1937, **36**, 388.

[3] *Refract. J.*, 1938, **14**, 690; *Trans. Brit. Cer. Soc.*, 1939, **38**, 304.

TABLE LXIII.—EFFECT OF TEMPERATURE ON SPECIFIC HEAT.[1]

Temperatures.	Specific Heats.	Averages of Concordant Results.
° C.		
700	0·253, 0·233, 0·262, 0·234, 0·233	0·233
830	0·242, 0·239	0·241
900	0·246, 0·245, 0·231	0·246
1000	0·264, 0·266, 0·249, 0·261, 0·267, 0·259	0·263
1100	0·258, 0·252	0·255
1150	0·261	0·261
1300	0·264	0·264

These correspond to

specific heat=0·193+0·00006t,
where t is the temperature in °C.

Bradshaw and Emery found an average specific heat of 0·284 between 0° and 1200° C., but various observers found the specific heat of kaolin to be only 0·205–0·225, though Navias found it to be 0·50–0·55.

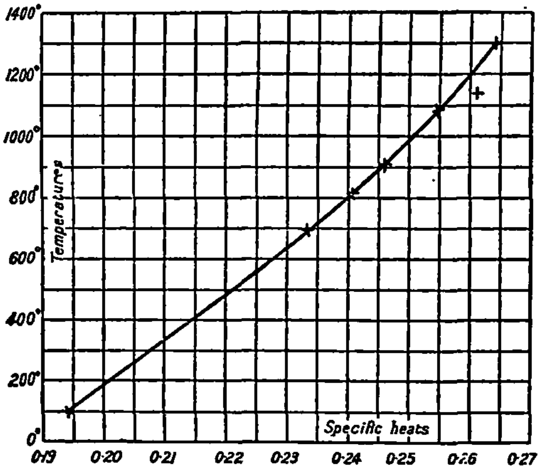

FIG. 92.—Mean specific heat of firebricks at temperatures up to 1300° C.

The *coefficient of heat-conductivity*[2] or of *thermal conductivity* of a material is the ratio of the rate of flow of the heat to the temperature-gradient (*i.e.* the fall in temperature per unit of length) in the material. The rate of flow is represented by Q/At, where Q is the total quantity of heat flowing across a face of area A in time t. The temperature gradient is $(\theta_2-\theta_1)/d$, where θ_2 and θ_1 are the temperatures of the hot and cold faces respectively, and d is the thickness of the material. Hence,

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[1] These results are plotted in fig. 92.

[2] The abbreviated form *heat conductivity* is often used.

$$\frac{Q}{At}=\frac{k(\theta_2-\theta_1)}{d}$$

or

$$k=\frac{Qd}{At(\theta_2-\theta_1)}$$

where k is the coefficient of conductivity; it can be expressed in either of the following forms, according to the units employed:[1]

cals./cm.^{2}/second/° C./cm. (c.g.s. units),
B.T.U.'s/ft.^{2}/hour/° F./in. (British units).

The term k is sometimes regarded as a constant, but it is only so within narrow ranges of temperature, and tends to increase with temperature for glassy and porous substances, so that, with most refractory materials, the thermal conductivity increases with the temperature. The chief exceptions are magnesite, silicon carbide, and graphite.

The coefficient of thermal conductivity of fireclay bricks varies with the clay used, the sizes and number of the pores, and the bulk-density of the material. In fireclay and silica bricks it averages 0·0035 c.g.s. units, but varies with the range of temperature through which it is measured.

The conductivity of bricks which have been made highly porous, *e.g.* by mixing fireclay with carbon dust and then burning out the latter, is only 0·0005, or one-sixth of that of ordinary fireclay bricks (see "Insulating Bricks").

The term "heat conductivity" only applies when the flow of heat is steady throughout the whole mass. If the temperature at each point in the mass varies with the time, the term *diffusivity* (p. 375) is employed.

The values of k for different refractory materials at different temperatures have been determined in various ways and by numerous investigators.[2]

TABLE LXIV.—HEAT CONDUCTIVITY (WOLOGDINE).

	Burned at	Conductivity.		Porosity Per Cent. by Vol.
		Kg. Cal. per Second per Sq. Cm. per Cm. Thickness, with a Temp. Diff. of 1° C.	Kg. Cal. per Hour[3] per Sq. M. per M. Thickness, with a Temp. Diff. of 1° C.	
	° C.			
Fireclay bricks .	1050	·0035	1·25	29·4
,, ,, .	1200	·0030	1·07	..
,, ,, .	1300	·0050	1·81	24·1
,, ,, .	1300	·0042	1·50	30·2
Fireclay retorts .	1300	·0038	1·37	27·3
Bauxite bricks .	1050	·0031	1·11	41·5
,, ,, .	1300	·0033	1·19	38·4
,, ,, .	1050	·0020	0·71	42·5
Silica bricks .	1350	·0031	1·12	42·9
,, ,, .	1050	·0058	2·08	35·1
Magnesia bricks .	1300	·0065	2·35	41·0
Chromite . .	..	·0066	2·37	..
Graphite . .	..	·0250	9·00	..
Kieselguhr . .	..	·0018	0·64	58·0
Hard porcelain .	1400	·0043	1·55	..

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[1] Other units may be employed if desired, *e.g.* B.T.U.'s/min./° F./in.

[2] See Cohn, *Ber. deut. ker. Ges.*, 1928, **9**, 242–6; and Norton, *Refractories*, 433–440, for the results of numerous determinations.

[3] The figures in this column are convenient when studying the thermal conductivity of thick masonry.

Owing to the difficulties involved and the assumptions which have been made the results differ greatly.

On heating fireclay bricks the thermal conductivity increases, and at 900° C. a pronounced increase occurs. Among the most accurate determinations of the thermal conductivity of various kinds of firebricks are the investigations of Wologdine in 1909, of Dougill, Hodsman, and Cobb in 1915, and of Dudley in the United States in 1915. These results are summarised in Tables LXIV., LXV., and LXVI.

S. M. Marshall has pointed out that Wologdine's results only apply to under-burned goods (*i.e.* those burned at or below 1350° C.), and that silica bricks burned at 1600° C. are, at this temperature, better heat conductors than fireclay bricks burned at 1300° C.

Wologdine's investigations were made on a disc 5 cm. thick, which formed the top of the furnace, and, as this disc had to be made specially, these results are not strictly comparable with those obtained with bricks or blocks of a different shape, or made in a different manner. The results are further vitiated by the absence of data as to the conditions under which the test-pieces were burned. These objections are overcome in the method used by Dougill, Hodsman, and Cobb, who used ordinary sizes of bricks, and determined the amount of heat passing through the test-piece by measuring the quantity of

TABLE LXV.—HEAT CONDUCTIVITY (DOUGILL, HODSMAN, AND COBB).

Specimen.	Chemical Analysis.	Thickness.	Apparent Sp. Gr.	True Sp. Gr.	P_a.[1]	P_b.[2]	Temperature Range of Measurement.		Mean k.[3]	Remarks.
							Lower Surface.	Upper Surface.		
		Ins.			Per Cent.	Per Cent.	Degrees.	Degrees.		
Fireclay brick (Farnley)	SiO_2 . . 66·0	1½	1·95	2·54	23·3	30·3	825	260	0·0029	Hard fired to Seger Cone 10–11 approximately.
	Al_2O_3 . . 31·0						970	300	0·0029	
	Fe_2O_3 . . 1·2						1080	330	0·0036	
	CaO . . 0·3						1440	550	0·0040	
	MgO . . 0·9	1½					1100	420	0·0033	Another specimen.
	Alk. . . 1·0						1350	510	0·0039	
Fireclay brick (Farnley)	as above	1½	1·90	2·67	28·7	40·4	1005		0·00165	Soft fired to Seger Cone 8–9 approximately.
							1020		0·00120	
Siliceous brick (Farnley)	SiO_2 . . 82·5	3	1·82	2·53	28·2	39·3	1300	310	0·0025	With many silica grains.
	Al_2O_3 . . 16·1									
	Fe_2O_3 . . 1·2									
	CaO & MgO Tr.									
	Alk. . . 1·3									
Silica brick (Gregory)	SiO_2 . . 95·3	2½	1·75	2·32	24·6	32·6	1240	440	0·0039	
	Al_2O_3 . . 2·0									
	FeO_2 . . 1·1	2½	1·74	2·32	24·8	..	995	295	0·0030	Another specimen. Both coarse grained.
	CaO . . 1·5									
							1210	370	0·0035	
							1395	440	0·0042	
Magnesia brick (Mabor)	SiO_2 . . 5·0	2½	2·40	3·51	31·4	45·9	380	270	0·0170	Finer grained than the above.
	Al_2O_3 . . 0·4						560	325	0·0151	
	Fe_2O_3 . . 1·6						600	400	0·0148	
	CaO . . 1·7						700	450	0·0132	
	MgO . . 92·1						750	470	0·0116	
							875	525	0·0110	
							1025	583	0·0101	
							1040	590	0·0098	
							1370	690	0·0091	

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[1] P_a is the ratio of the volume of the pores to the total volume of the brick.

[2] P_b is the ratio of the volume of the pores to the volume of the solid portion of the brick.

[3] k is the thermal conductivity in gramme-calories per second per degree Centigrade for a cube of 1 cm.

water evaporated from a calorimeter placed above it, the temperature of the top of the brick being determined by an electric pyrometer.[1]

The chemical analysis and porosity data were not derived from measurements on the actual test brick, but on similar specimens of the same make.

It should be noted that in Table LXVI. *k* is in gramme-calories per second per *inch* cube, whilst those in the two previous tables are calculated on 1 *cm.* cube.

TABLE LXVI.—HEAT CONDUCTIVITY (BOYD DUDLEY).

Analysis of Bricks.

	Woodland. Per Cent.[2]	Quartzite. Per Cent.[3]	Star Silica. Per Cent.[4]	Magnesite. Per Cent.
SiO_2	52·93	73·91	95·85	2·50
Al_2O_3	42·69	22·87	0·88	0·50
Fe_2O_3	1·98	1·48	0·79	7·00
CaO	0·33	0·29	1·90	2·75
MgO	0·38	0·31	0·14	86·50
Alkalies	1·55	1·20	0·39	..
Loss on ignition	..	..	..	0·10
Apparent density	1·91	1·91	1·56	2·46

Heat Conductivities of Bricks.[5]

Material.	Test No.	Exp. Temp. Range.	Mean *k* over Exp. Range.	Calc. *k* at 100°.	Calc. *k* at 1000°.	Average *k* at 100°.	Average *k* at 1000°.
Woodland	1	120 to 965	0·00676	0·00532	0·00816	0·0043	0·0086
„	2	100 „ 1025	0·00666	0·00438	0·00880	0·0043	0·0086
„	3	400 „ 995	0·00704	0·00332	0·00886	0·0051	0·0086
Quartzite	1	100 „ 935	0·00679	0·00504	0·00880	0·0051	0·0086
„	2	100 „ 960	0·00670	0·00521	0·00836	0·0056	0·0108
Star silica	1	100 „ 910	0·00794	0·00561	0·0108	..	..
Magnesite	1	445 „ 830	0·0343	..	0·0343	..	0·0343

These results show that the silica blocks tested had a lower heat conductivity than the clay ones—a result which is opposed to the statements of several well-known engineers, though the latter have not published the data on which their statements are based. It is not improbable that these widely differing statements on the heat conductivity of refractory materials may be largely due to variations in the porosity of the materials used.

It is instructive to compare the foregoing results with each other, though in all probability those in Table LXV. are the most likely to agree with conditions of use.

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[1] A complete description of the apparatus used and some of the precautions necessary to secure correct results are given in *Journ. Soc. Chem. Ind.*, 1915, 465.

[2] Woodland firebricks are made of fireclay.

[3] These quartzite bricks are made of silica with a clay bond.

[4] These are made of silica with a lime bond.

[5] Dudley's results agree closely with those obtained by G. F. Brown (*Trans. Amer. Cer. Soc.*, 1914, **16**, 382), who used cylindrical blocks of material with a thermocouple near each end.

Fireclay bricks are at all times bad conductors of heat, but have a high power of radiation; hence, articles placed in chambers built of fireclay bricks may be heated intensely, in spite of the low conductivity of the bricks used.

It should be remembered that the results of thermal conductivity tests on single bricks in a test-furnace do not strictly give results comparable to those obtained when the same bricks are used in a furnace. For example, the deposit of carbon which forms in a coke oven, and the semi-fused slags, etc., which form in other kilns and furnaces, materially affect the conductivity of the bricks. Unfortunately, there is very little information on the actual thermal conductivity of firebricks when *in situ*, so that it is almost impossible to take into consideration the difference between the thermal conductivity of a firebrick as found experimentally and that of the brick when in actual use.

Firebricks, when in use in a reducing atmosphere, soon become coated with carbon, which greatly alters their thermal conductivity, so that laboratory tests of the thermal conductivity are not of much value.

H. Oliver[1] has found that the differences in the values of the thermal conductivity of identical diatomaceous insulating materials found by different investigators are so large as to be very unsatisfactory.

Thermal Conductivity and Temperature.—The thermal conductivity of refractory materials varies with the temperature as follows:[2]

Fireclay bricks.—The conductivity rises steadily from 0·8 at 300° C. to 0·95 at 1100° C. (In bricks of low porosity it rises from 1·1 at 1100° C.)

Silica bricks.—The conductivity depends on the porosity; it rises steadily from 0·8 to 1·3, bricks of low porosity having the greater conductivity.

Sillimanite bricks (with 20 per cent. of pores).—The conductivity falls steadily from 1·4 at 300° C. to 1·25 at 1100° C.

Grog bricks (with 60 per cent. of pores).—The conductivity rises steadily from 0·25 at 300° C. to 0·4 at 1000° C.

Corundum bricks (containing 25 per cent. of clay).—The conductivity falls steadily from 2·1 at 300° C. to 1·8 at 800° C. and 1·77 at 1100° C.

Magnesite bricks.—The conductivity falls steadily from 10 at 300° C. to 3 at 1100° C.

Chrome-magnesite bricks.—The conductivity falls steadily from 2·0 at 300° C. to 1·5 at 600° C.

Silicon carbide bricks.—The conductivity falls from 11–13 at 300° C. to 5–9 at 1100° C.; it depends on the porosity.

These figures are only approximate, but give a clear idea of the variations of the conductivity with temperature.

Diffusivity.—When the temperature in a material changes with time, as when heating up a furnace, the distribution of the temperature depends on the heat-capacity as well as on the thermal conductivity. The rate at which a heat-wave is transmitted through a material is termed the *diffusivity*. It is proportional to the conductivity and also to the specific heat and density of the material, so that two substances can have the same diffusivity and yet have different coefficients of heat conductivity.

The diffusivity (D) is conveniently expressed as the ratio of the thermal conductivity (k) to the heat capacity of unit volume (c) of the mass, so that

$$D=\frac{k}{c} \quad \text{or} \quad D=\frac{k}{sd},$$

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[1] *Trans. Cer. Soc.*, 1938, 37, 49.

[2] The conductivity is expressed in kilocalories per metre per hour per degree C.

where s is the specific heat and d is the bulk-density of the material, all in c.g.s. units.

For fireclay brick walls, 9 in. or more in thickness, the diffusivity is 0 025 for most working temperatures, and if the time required for the heat inflow to balance the heat outflow is t hours, whilst the wall is d in. thick, $t=\frac{d^2}{8}$. For thinner walls, $t=\frac{d^2}{5}$. The diffusivity is independent of the porosity.

Heat Radiation.—It is commonly assumed that the radiation (or emission) of heat from the interior of a furnace corresponds to that of a black body and obeys Stefan's law, but Heilmann[1] has found that the emissivity of light-coloured bricks falls off rapidly as the temperature increases, and at 1600° C. and above it may be only 40 per cent. (or less) of that of a black body. He suggests that where high emissivity is needed, so as to transfer heat from the walls and crown of a furnace to the contents, the furnace should be lined with dark-coloured bricks, but where a slow heating of the contents is desired, light-coloured bricks are best. When the contents have reached the same temperature as the walls, the effect of radiation may be ignored.

The *electrical resistivity* of fireclay bricks is, according to Hartmann, Sullivan, and Allen,[2] as follows :—

Cold	Less than	137,000,000	ohms per cubic cm.
800° C.	,,	57,600	,, ,,
900° C.	,,	20,600	,, ,,
1000° C.	,,	10,800	,, ,,
1100° C.	,,	6,590	,, ,,
1200° C.	,,	4,160	,, ,,
1300° C.	,,	2,460	,, ,,
1400° C.	,,	1,420	,, ,,
1500° C.	,,	890	,, ,,

Stansfield, M'Leod, and M'Mahon give the following figures of electrical resistivity for temperatures between 1000° C. and 1550° C. :—

1300° C.	1300	microhms per c.c.
1400° C.	690	,, ,,
1500° C.	280	,, ,,
1550° C.	60	,, ,,

The electrical resistivity of fireclay bricks is reduced by impurities in the bricks and by a reduction in porosity.

Between 700° C. and 900° C. the specific electric resistance is as high as porcelain, but less than that of quartz and recrystallised alumina.[3]

The specific electrical resistance of fireclay bricks is usually given by[4]

$$S=e^{\frac{B}{T}+A},$$

where S is the specific electrical resistance, T the absolute temperature, and A and B are constants for the particular material.

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[1] *Mechanical Engineering*, 1936, p. 291.

[2] *Trans. Amer. Electrochem. Soc.*, 1920, **38**, 279.

[3] Komarkow and Tarejew, *Ogneupory N.*, 1937, **9**, 619–23.

[4] *J. Amer. Cer. Soc.*, 1924, **7**, 764.

The electrical conductivity of fireclay bricks increases with rise in temperature and is moderately high in hot bricks, though not sufficiently good to make them useful conductors.

The following electrical resistivities were determined by A. V. Henry :—[1]

All after calcination at 1500° C.	Ohm-cms.					
	300° C.	500° C.	800° C.	1000° C.	1200° C.	1500° C.
Kaolin . .	133×10^5	269×10^3	14,600	3,910	1,460	681
Sillimanite .	..	607×10^4	179,000	36,300	11,500	3,150
Silica . .	..	113×10^5	300,000	49,000	15,700	5,660
Magnesite .	..	..	330×10^5	478×10^4	94,700	615
Diaspore .	..	462×10^3	12,700	2,920	886	..

Industrial Requirements.—Industrially, the most important properties of fireclay bricks are concerned with their resistance to heat, abrasion, and materials which combine with them (alkalies and bases), especially when the bricks are in continuous use or are repeatedly heated and cooled. In most cases, it is essential that the bricks should not spall, peel, or crack with sudden changes of temperature ; that they should not shrink unduly so as to endanger the safety of the structure of which they form a part, and that they should prove reasonably durable under the conditions of use.

In addition to a close surface, some industrial conditions call for a brick which is close-textured throughout. It is then necessary to use firebricks made of highly aluminous clays which will vitrify at a moderate temperature, but will not lose their shape at the temperature at which they are to be used. Clays of this type are not, at present, extensively used in this country.

From the foregoing statements, it will readily be understood that the durability of fireclay bricks in use depends upon a multiplicity of factors, physical and chemical, some of which are not clearly understood.

These factors may be arranged in three groups—

(1) Those concerned with the manufacture of the bricks. (The maker's responsibility.)

(2) Those concerned with the laying of the bricks. (The builder's responsibility.)

(3) Those concerned with the use of the bricks. (The user's responsibility.)

The problem is complicated by the fact that the three groups are generally controlled by three different sets of men, and to a large extent each of these understands only one group of factors. Thus, if the brick manufacturer thoroughly understood the nature of the conditions his bricks would have to withstand, or if the user knew what method of manufacture would best meet his conditions, the matter would be greatly simplified. At present this is not the case.

So far as the manufacturer is concerned, the chief causes of defective fireclay bricks are :

(*a*) neglect of careful selection and purification ;

(*b*) the use of too little grog ;

(*c*) the use of unsuitable grog ;

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[1] *J. Amer. Cer. Soc.*, 1924, **7**, 764.

(*d*) mechanically inefficient methods of crushing and mixing;
(*e*) inadequate grading, or the use of particles of unsuitable sizes;
(*f*) unsuitable conditions of pressing, including maladjustment of the presses;
(*g*) irregular drying; and
(*h*) irregular burning, including insufficient burning.

These defects result in the following:—

(i) the refractoriness of the product is low;
(ii) the refractoriness-under-load is low;
(iii) the bricks are irregular in size;
(iv) the bricks are too porous;
(v) the bricks contain minute fissures and laminations;
(vi) the bricks have a low resistance to abrasion and to slags; and
(vii) the bricks are too sensitive to rapid changes in temperature.

By the exercise of sufficient knowledge and skill, these defects may be avoided. It will then be found that the most durable fireclay bricks have (i) a high apparent density, (ii) great resistance to slag, (iii) ample resistance to crushing, and (iv) constancy of volume when heated and cooled.

In the user's group (see (3), p. 377) the durability of fireclay bricks is chiefly diminished by—

(i) Simple fusion of the bricks, owing to the temperature being higher than they can endure. The remedy consists in using more refractory bricks.

(ii) Chemical and abrasive action of slags or alkaline or basic substances.

(iii) Chemical action of gases.

Among defects which are more largely due to the manufacturer may be mentioned—

(iv) The bricks may deteriorate rapidly by spalling or breaking up into splinters, owing to the texture being insufficiently felted.

(v) Excessive porosity will permit fire-gases to penetrate into the interior and set up reactions, which may have serious results, as in (iii). Highly porous bricks also permit dust, slag, etc., to penetrate and act as in (ii).

(vi) Mechanical weakness, due to improper composition or imperfect burning. The latter will cause excessive shrinkage, open joints, irregular pressure, deformation under load, and leakage.

So far as durability is concerned, the best fireclay brick is one which is sufficiently heat-resisting to retain its shape indefinitely at the highest temperature to which it will be exposed in use; it will offer so dense an outer surface that little corrosion or abrasion can occur, and the texture of its interior will be such as to prevent it spalling or cracking when exposed to sudden changes in temperature.

For further information on the influence of the builder and user on the durability of firebricks, see Chapter XVIII. (Furnace Linings, etc.).

It is highly important to observe that high-grade firebricks can only be made by the closest attention to details, not only in manufacture, but in storage. It is not enough to consider that a clay deposit which has proved good for the past thirty years is equally good to-day, nor that a particular mixture of clays must for ever remain suited to the needs of any one class of firebrick users. Conditions change, requirements are more varied, and the tests are more severe than those of ten or twenty years ago, and if modern firebrick manufacturers still wish their products to deserve the name "high-grade," they must not rest content with their achievements in the past.

Even under favourable conditions of manufacture it is necessary to exercise the greatest care in the management of the works in order to produce the bricks at a profit.

GROG FIREBRICKS.

In Great Britain the extensive use of large proportions of grog in firebricks has never become popular. The reason is simple, viz. that manufacturers have hitherto been able to supply their customers with bricks made almost exclusively of fireclay, as described on pp. 248 to 337. Large proportions of grog cannot be added to these fireclays, as they have not sufficient binding power.

With increasing stringency in the demands of metallurgists and others, and especially in view of the fact that bricks made chiefly of grog and imported from abroad have proved more serviceable than fireclay bricks in several important instances, it is questionable whether British manufacturers may not have to take increased interest in the production of grog bricks. Indeed, some of them have done so for some time, and the advantage, formerly, of using some German fireclay bricks has, by this means, been met.

Uses.—Grog bricks are used for the same purposes as the highest grades of fireclay bricks, and for parts of furnaces, ovens, retorts, etc., for which fireclay bricks are not satisfactory on account of their shrinkage, or tendency to spall when exposed to sudden changes in temperature. They may be used in almost all cases where silica bricks are not satisfactory, but to ensure satisfactory results, it is necessary to vary the size or "grade" of the grog particles and the proportion of bond to suit particular requirements.

They are particularly suitable for furnaces working at the highest temperatures, as in steel-making, and where great resistance to slags is essential or where there are sudden changes in temperature. They are specially used for the construction of furnaces for the iron and steel industries, also in lime, cement, brick, tile, and pottery kilns, in glass-melting furnaces, in retorts and coke ovens, and in furnaces for refining zinc, lead, copper, and other metals, and for the production of glazes and other molten material. For boiler flues and other purposes where the conditions are less severe, fireclay bricks are equally satisfactory, and can be made more cheaply.

Materials.—As their name implies, the chief constituent of grog bricks is *grog*. This is produced by burning high-grade fireclays, selecting the cleanest portions of the burned product, and grinding it to a coarse powder. The grog is then mixed with a suitable proportion of highly plastic clay—usually a ball clay—and water so as to bind the particles together into a homogeneous mass. This paste is made into bricks by any of the methods described on pp. 277 to 289, and is burned in a similar manner. Hence, the essential differences between grog bricks and fireclay bricks do not lie in the machinery or kilns used, but in the composition of the paste of which the bricks are made. In the case of fireclay bricks, this paste is largely composed of a lean clay which shrinks considerably on drying and burning, whereas grog bricks are chiefly made of grog which does not shrink, and the proportion of clay in them is relatively small.

The use of the term "grog" for *sand*, *sawdust*, and other non-plastic materials is undesirable.

The *grog* should be made of the best qualities of fireclay, as described on p. 140.[1] Crushed firebricks should not be used unless in very exceptional cases. The selected grog should be crushed and screened so as to separate pieces of various sizes, these being selected according to the particular purpose for which the bricks are to be used, so as to produce the best result in each

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[1] Grog dust must not be used except for special purposes. The use of the dust accumulated in hot-blast stoves and boiler flues, as grog, was patented by C. H. Aston, 1891, but it is usually too fine and too contaminated with fluxes to be of much value as a refractory material.

case. It is not desirable to employ a larger proportion of fine grog than is really necessary, because when much fine grog is present the refractoriness of the resultant bricks and the resistance to sudden changes in temperature will be reduced. On the other hand, an excess of coarse grog is undesirable, as it causes excessive shrinkage due to a weak structure, so that the bricks will not withstand a heavy load, and show a tendency to crack.

The use of ground fireclay compressed into blocks under a pressure of 200 lb. per sq. in., burned, and then ground and screened was patented in 1929 (Eng. Pat. 329,803). The objections to such grog are stated on p. 141.

Grog made by burning lumps of raw fireclay is much superior to grog made from ground clay which has been made into bricks before being burned. The use of sillimanite, cyanite, chromite, carborundum, zirconium, magnesite, dolomite, and ground saggers or bricks as grog is claimed in Eng. Pat. 262,383 (1925). At one time, only "fully burned grog" (*i.e.* grog burned at 1250°–1380° C.) was used, but it is now common to use grog burned at only 1000° C. This does not possess the same properties as grog burned at a much higher temperature and is, on the whole, inferior. On the other hand, if grog is first calcined at 600° C., various impurities can be removed by electro-magnets which cannot be separated from grog burned at a higher temperature. After such separation the grog can be burned at 1500° C. or above; the cost of the double burning is generally regarded as prohibitive.

The use of grog composed of (*a*) particles larger than 3 mm., and (*b*) less than 1 mm., but with no intermediate sizes, in conjunction with a clay-slip, was patented in 1934 (Eng. Pat. 427,781). The use of grog of other sizes was patented in Eng. Pat. 438,794 (1934). The use of 45–65 per cent. of grog particles between 3- and 30-mesh and of 55–35 per cent. of grog passing through a 50-mesh sieve (but not with intermediate particles) was patented in 1930 (Eng. Pat. 364,311; see also Eng. Pat. 370,435).

It is generally found that the largest pieces should not exceed ⅛ in. in diameter, though for very large masses ¼-in. or even ½-in. pieces may be used satisfactorily.

The best results are obtained with a moderate proportion of coarse grog, sufficient medium-sized pieces to fill the larger interstices between the coarser particles, sufficient rather fine grog to fill the remaining interstices, and enough clay to coat all the particles and unite them (see p. 382).

The use of an excess of medium-sized grog results in a weak product, because it does not merely fill the interstices, but separates the particles and creates fresh interstices. The use of too much fine material results in spalling. The best means for preventing this is to omit the middle grain-sizes, using only a mixture of fairly coarse grog and a minimum of (fine) clay. Three sizes of grains are usually ample, *e.g.*

mm.	in.
0–3	0–0·125
3–6	0·125–0·250
6–10	0·250–0·500

It is generally best to omit the 0·5–2·0 mm. (0·02–0·08 in.) particles from the grog, but the use of fine grog is more popular on the Continent than in this country.

The grog and clay should be ground separately and screened or graded separately, as otherwise an accurate grading of the grog is impossible. The slight additional cost of the separate treatment is more than repaid by the improvement in quality and the reduced waste.

When a satisfactory mixture has been obtained, it is passed through various sieves of increasing fineness in succession and the proportion remaining on each noted. In future mixings the same test is carried out, and any notable variation is inquired into and the variation stopped. Such variation is usually due to something wrong with the mills or riddles, though occasionally it may be due to the introduction of a different clay.

It is desirable to test the ground materials, both before and after mixing, as this gives a more rapid clue to the source of variation when such variation occurs. The test need only take a few minutes, as about two pounds is ample for a test if a fairly accurate pair of scales is used for weighing the different portions of clay, whilst if a kilogramme of clay (or mixture) be used and the proportions on the sieves weighed in grammes, the percentage of each may be found with a minimum of calculation. After being weighed or measured the grog should be *thoroughly* soaked in water. This is preferable to soaking the mixture of clay and grog. The wetness of the grog is important.[1]

The *binding clay* should have a high degree of plasticity, and it should vitrify at as low a temperature as possible (usually about 1000° C. to 1200° C.), but should not begin to lose its shape until heated to Seger Cone 26, or to a higher temperature. The plasticity and range of vitrification are both essential in order that the clay may efficiently bind the particles of grog securely together. Devonshire ball clays are among the best British clays for this purpose, but certain clays from Dorset, Derbyshire, Yorkshire, Staffordshire, Warwickshire, Wales, and other localities will serve equally well. The binding clay must suit the grog used, and must not shrink unduly. If the two do not unite well, the product will be weak and friable. It is particularly necessary to grade very carefully when a highly plastic clay is used, as otherwise it shrinks and cracks, forming very weak bricks. When only a small proportion of binding clay is used it should be made into a slip with water and then added to the previously soaked grog. When a larger proportion of clay is used it is often an advantage to make a portion of the clay into a slip, mix it well with the soaked grog, and then mix the product with the remainder of the clay.

Hugill and Rees [2] have found that grog bricks containing less than 10 per cent. of ball clay as binder are often more durable than ordinary fireclay bricks and never less durable. The best results were obtained by adding the binder in the form of a slip and tempering the mixture in a pan-mill. Deflocculated -clay-slip gave a greater refractoriness-under-load, but the bricks were difficult to mould.

The use of alkali in making the slip is beneficial.[3] About 0·05 per cent. of the weight of the binding clay should be the maximum amount of alkali used; 0·02 is usually better.

The use of fireclay mixed with silicic acid as a binder was patented in 1923 (Eng. Pat. 218,495). The use of 1–5 per cent. of sodium meta-aluminate as a binding agent was patented in 1933 (Eng. Pat. 444,323). The conversion of a small proportion of the grog or clay into the colloidal state and its use as a binder were patented in 1926 (Eng. Pat. 264,192).

Bentonite appears to be a useful binder in bricks made chiefly of grog. About 6 per cent. of bentonite to 94 per cent. of grog is usually suitable. The use of 10 per cent. (or less) of alkaline silicates such as glass or slag, in addition to grog, in order to strengthen the bricks, was patented in 1927 (Eng. Pat. 286,677).

Heating the grog in water containing a deflocculating agent (alkali,

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[1] The use of wet grog without any binder was patented in 1932 (Eng. Pat. 397,977).

[2] *Trans. Cer. Soc.*, 1931, **30**, 353.

[3] See Eng. Pat. 253,947 (1925).

water-glass, etc.) before adding the clay was patented in 1930 (Eng. Pat. 368,858).

It has been suggested that ferric oxide—when added to the bricks and the burning of the latter is finished under reducing conditions—is one of the best binders for grog bricks, especially where it is in association with a clay. In Germany, a ferruginous binding clay has been used successfully for some years.

Messrs. J. H. Sankey & Son have patented the use of sodium silicate as a binder in the manufacture of bricks exclusively from grog, no raw clay being used. These bricks neither expand nor shrink when in use, and as almost the whole of the material has previously been calcined, they are more stable at high temperatures than many fireclay bricks.

The **proportions** of grog and clay to be used depend on the grading of the former and on the binding power of the latter. So long as the bricks obtained are sufficiently strong and durable in use, the smaller the proportion of clay the better. Grog bricks which are rich in clay have a closer texture than others, but are more liable to splinter and spall when exposed to abrupt changes in temperature.

It is seldom that less than 1 part of fireclay[1] to 5 of grog can be used, as the bricks would lack mechanical strength; on the other hand, it is seldom necessary to use more than 1 part of clay to 2 parts of grog. Within these limits the manufacturer must usually ascertain by trial the proportions most suitable to his materials. Much smaller proportions of other clays have been used, in some cases only 5 per cent. being employed, this giving a ratio of 19 : 1. G. W. Mottram also claims to have found that 90 per cent. of grog and 10 per cent. of fireclay will give satisfactory results, provided the raw clay *is ground to a fine slip with two or three times its weight of grog and the* mixture added to the remainder of the ground grog. Deidesheimer and Jurschina, in 1908, patented the use of 96 to 99 parts of grog to 1 to 4 parts of clay. This mixture appears to have too little clay in it to be useful for most purposes for which grog bricks are used, unless the plasticity of clay is artificially increased.

The best grog bricks are made by using three sizes of grog, *viz.* "coarse," "medium" and "fine," but avoiding "dust." The proportions cannot be stated in advance, but should be such that the interstices between the particles of coarse should be filled by particles of medium grog, and the interstices in the mixture should be filled with fine grog. Coarse, medium, and fine grog in the proportions 1 : 2 : 1 are used in some works, but this fixed proportion is too empirical to be of general application. If the proportion of clay present is insufficient to fill the interstices between the particles of grog, the material *will not be sufficiently plastic to "work" satisfactorily.*

I. Albon and W. R. Parker in 1908 patented the use of a mixture consisting of 80 parts of finely ground grog produced from old firebricks, 10 parts of fresh fireclay, and 10 parts of fine sand. The disadvantage of this mixture lies in the use of old bricks which tend to include too much slag or fused material to be really satisfactory, and in the addition of sand which reduces the refractoriness of the material without conferring any particular advantage (other than cheapness) not obtained by the use of an equal weight of grog.

The ideal proportions of grog and clay consist of just sufficient clay to fill the voids between the grog particles (fig. 93, A); any more than this will do harm. It is a common mistake to use too much clay (fig. 93, B).

The *water* required will be about one-fifth of the weight of the grog and clay, but it varies greatly with the porosity of the grog. The addition of an

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[1] See p. 252 for other proportions of fireclay and grog.

unnecessary quantity of water should be avoided, as it tends to produce bricks with a loose and weak texture.

Where *accurate proportioning* is essential, the clay or clays and the grog should be dried before use, and the various materials should be weighed rather than measured.

The **mixing** of grog, clay, and water to form a paste is best effected in three stages:[1] (i) the grog and clay may be measured out in suitable proportions either by hand or in an automatic feeder; (ii) the grog is next saturated with water and is then roughly mixed with the clay; (iii) the remainder of the water may then be added and the whole of the materials mixed in a trough, pug mill, or pan mill, as described on p. 272. As it is highly important that the particles of grog should not be crushed, and that a thoroughly homogeneous paste should be produced, a well-adjusted trough mill or a tempering mill will usually be found the most satisfactory machine for the purpose. The use of such machines are described on pp. 273 to 277.

Where firebricks of an exceptionally high quality are required, the wet grog and clay are placed on a clean floor and hand-mixed by means of wooden spades, the mixture being sprinkled with water and repeatedly turned over. Three separate beds of mixture are made, so that whilst one is being formed another is souring, and the third is being sent to the pug mill to undergo a further mixture.

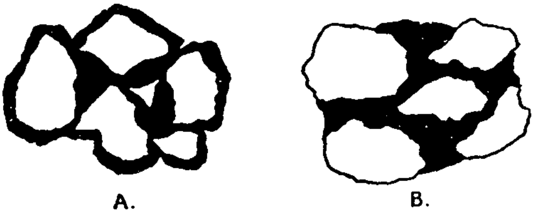

FIG. 93.—Mixtures of clay and grog.

If desired, the paste may be passed two, three, or even four times through the pug mill so as to ensure it being thoroughly mixed.

The blades of the mixer or pug mill and the pan of the tempering mill wear away rapidly when grog bricks are manufactured, and care must be taken to keep these parts of the machinery in a good state of repair.

Instead of mixing the materials with water, the binding material may be reduced to a colloidal sol and *sprayed* on to the grog (Eng. Pat. 370,477—1930).

Souring.—For grog bricks of the best quality the paste should be kept in a cool place and covered with wet bags so that it may sour. After a week's storage, during which no drying must be permitted, the paste is again passed through the pug-mill. The souring is less necessary if a de-airing machine is used. During the souring period the water distributes itself uniformly; it also produces the maximum plasticity attainable in the time allowed.

The **shaping** of grog bricks is effected by hand-moulding or by machines in the same manner as fireclay bricks, except that the moulders should wear gloves to prevent the grog unduly damaging the skin. Some manufacturers prefer to use a "sand-moulding" method for hand-made bricks. In this case, the moulder sprinkles a little grog-dust on half his bench, cuts off a suitable quantity of paste with a small hand-spade, and rolls or kneads this

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[1] In some firebrick works the grog is crushed to pieces not larger than walnuts, mixed with a suitable proportion of binding clay, and fed into an open edge-runner mill with a perforated pan, the openings in which are ⅛-inch diameter. No grading or screening is attempted, and the material discharged by the mill is simply mixed with water in a pug mill. This method of working saves expense, but the product, though commanding a ready sale, is not as satisfactory as that in which a well-graded grog is used.

into a clot of convenient size and shape. In doing this he must avoid including any hard lumps of partially dried material. The clot is raised and dashed down on the bench several times so as to make it compact, and it is then lifted well above the moulder's head and thrown with great force into the mould, the latter having been prepared by dipping it in water and then in grog dust. The corners are well filled by the moulder inserting his thumbs, and the superfluous material is afterwards cut off with a straight-edge or wire. A little grog dust is strewn on top of the mould. A carry-off boy then lays a pallet board on the mould and takes the latter with its contents to the drying floor. Here he turns the mould, deposits the brick, and returns to the moulder. The objection to this method is that if any grog becomes enclosed in the clot—and unless exceptional care is taken this is sure to occur—the bricks will tend to crack along the lines of grog. Hence, slop-moulding with as stiff a paste as possible is a preferable method.

Machine-made grog bricks are made precisely as described on p. 278, and the same conditions apply to them. The grog being harder and more abrasive than raw clay, the dies wear away much more rapidly than when clay bricks are being made.

The effect of pressure is to break down the larger particles and to form a mixture of maximum density, which in the case of a dry mixture consists of 40 per cent. of material coarser than 20-mesh and 40 per cent. finer than 100-mesh, the remaining 20 per cent. being fairly uniformly distributed between the 20-mesh and the 80-mesh sizes. The density is greatly increased by pressure up to a limit of about 3 tons per sq. in. Any further increase in pressure has only a small effect on the density and is, to a large extent, wasted.

Tamping or *ramming* instead of pressing, as a means of shaping grog bricks, has received much attention and is mentioned in various patent specifications. It is very suitable for large blocks and for crucibles, but is too costly to be used for grog bricks.

Slip-casting can also be used for large blocks, but is too costly for bricks (see Chapter XII.).

When bricks are made by tamping, ramming, or slip-casting it is not difficult to include 85–90 per cent. of grog, whereas with more plastic processes only a much smaller proportion can be used.

Drying is effected by the same means as those used for fireclay bricks, but it may usually be carried out rather more rapidly on account of the larger proportion of non-plastic material in grog bricks.

Setting and **burning** are carried out as described on pp. 293 to 337, the same kinds of kilns being used.

The burning of grog bricks differs from that of fireclay bricks because (the grog having been burned previous to use) the burning of the bricks is only needed to mature the bond. In ordinary fireclay bricks, on the contrary, part of the purpose of burning is to heat the whole material sufficiently to make it as constant as possible in volume when in use, and also to produce sufficient vitrified or fused material to act as a bond. Consequently, grog bricks may be burned more rapidly than fireclay bricks.

The **properties** of grog firebricks are similar in many respects to those of fireclay bricks, but they have the following advantages:—

(*a*) Grog bricks are often more refractory, as the impurities are more readily observable in the grog than in the raw clay, and can be removed more completely. Some of the alkalies have also been volatilised.

(*b*) The use of carefully graded grog reduces the likelihood of the bricks spalling, splintering, or cracking when exposed to sudden changes in temperature.

(*c*) Grog bricks shrink much less in use than fireclay bricks, as the grog has been calcined once before use, and again in the form of bricks, so that, if properly made, the shrinkage of grog bricks should be negligible. Moreover, little or no harm results from over-firing the grog, whilst an excessive temperature would cause bricks to lose their shape. Hence, the grog can be burned to a far higher temperature than it is likely to reach when the bricks are used, and yet bricks made of grog can be burned in course of manufacture at a temperature at which there is little risk of their being misshapen.

(*d*) The chemical composition of grog bricks depends on that of the grog and bond clay of which they are made. As the purest clays known contain, when burned, 46 per cent. of alumina, any brick containing a larger proportion than this must have been made of bauxite or other highly aluminous mineral (see Chapter V.).

(*e*) The crushing strength is usually higher than that of fireclay bricks, and the shrinkage on reheating less.

(*f*) Grog bricks are less tender than bricks made wholly of raw clay and can, therefore, be dried and burned more rapidly than the best fireclay bricks. Grog bricks should be harder burned than ordinary fireclay bricks, the individual particles should be sharp or angular and the bricks should show by their texture, colour, and hardness that they have been uniformly burned.

As compared with fireclay bricks, the disadvantages of grog bricks are—

(i) Grog bricks sometimes have rather less crushing strength, but this only occurs when the binding clay has too short a range of vitrification, or when the bricks are specially porous.

(ii) Grog bricks are sometimes more porous than fireclay bricks, but as this is due to using an under-fired grog, too little binding clay, or to under-firing the bricks, it can easily be avoided if desired.

(iii) The cost of manufacture of grog bricks is higher in Great Britain than abroad, as on the Continent there is usually an ample supply of broken saggers from the porcelain works. These saggers are bought at a cheap rate and are used as grog. For bricks of specially good quality, however, the grog is made from selected clay burned in special kilns, so that for the highest class of bricks the cost of manufacture is similar to that in this country.

(iv) When grog and plastic clay are mixed the particles of clay tend to coat those of grog and the latter draw water from the clay. On applying a vacuum, air is drawn from the pores in the grog and in escaping tends to crack the surrounding clay, so that instead of greater strength a weaker mass is produced by de-airing. If the grog is fully non-porous this defect cannot occur.

BRICKS OF FUSED CLAY.

Bricks may be made by heating clay and then fusing it in an electric arc, the molten product being poured into moulds. Such bricks are very dense and resistant to corrosion. They are manufactured by the Corhart Refractories Co., Louisville, Kentucky, U.S.A., and their use is rapidly increasing in spite of their cost.

SILLIMANITE BRICKS.[1]

The term *sillimanite bricks* is applied indiscriminately to bricks made from cyanite, sillimanite and andalusite and from a mixture of fireclay and bauxite.

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[1] This term should be restricted to bricks made of sillimanite, but this restriction is not observed in commerce, as some of the largest manufacturers of sillimanite bricks use cyanite as their raw material, and all contain mullite rather than sillimanite if they have been properly burned.

All these substances are converted into mullite when heated, so that the term *mullite bricks* would be more appropriate. The erroneous use of the term sillimanite arose from the mistaken idea that the crystals in the heated product were sillimanite, whereas, in fact, they were mullite; though the product obtained by heating cyanite to a red heat may be sillimanite, and this, on heating to a higher temperature, becomes converted into mullite. The term *sillimanite bricks* is now so extensively used in commerce, however, that it must, probably, be accepted, even when it is applied to bricks made of other minerals. In the present volume it is used in its commercial sense, though care has been taken, where possible, to state clearly which mineral has been used. The term *artificial sillimanite* is equally erroneous; it should be *artificial mullite*. *Natural mullite* is described on p. 147. *Artificial mullite* is formed:

(*a*) When cyanite, sillimanite or andalusite is heated to 1200° C., though for proper development of the crystals a higher temperature is usually needed. The commercial sillimanite used in this country is made chiefly in this manner. An electric furnace, a shaft-kiln, a rotary kiln or even a short tunnel-kiln may be used for this purpose. The temperature attained should be as near 1500° C. as practicable, as the conversion is slow at lower temperatures.[1]

(*b*) When a mixture of clay and alumina in suitable proportions is heated to 1400° C. or above. The reaction may be represented by the equation:

$$Al_2O_3.2SiO_2.2H_2O+2Al_2O_3=3Al_2O_3.2SiO_2+2H_2O.$$

For the purest mullite, a pure kaolin or china clay and pure alumina must be used, as in the manufacture of Marquardt porcelain, but for most purposes a fireclay and white bauxite are used.

The heating may be effected in an electric furnace (Eng. Pats. 702—1907, 289,560—1927, and 345,236—1929), a shaft-kiln or a blast furnace.

The last is the invention of A. Malinovsky, who has developed a process for the manufacture of mullite on a commercial scale by heating a mixture of raw clay and coke in a specially constructed cupola or blast furnace, using compressed air at about 3 to 6 lbs. pressure. By this means the excess of silica is volatilised (it is probably reduced first to silicon carbide, then to silicon, which ignites spontaneously with great evolution of heat).

The furnace consists of a vertical cylinder of suitable size, into which is placed a little glowing coal, which is caused to burn more rapidly by the application of a blast of air, the furnace being meanwhile filled gradually with the material to be heated. After heating for about three hours, the contents of the cupola begin to boil, the furnace roars, and for about two hours the silica volatilises in dense bluish and finally brown fumes, after which the air blast is continued to produce a porous mass of specific gravity 2·62 to 2·86, which is then allowed to cool. The process occupies about seven hours, five or six hours being taken in bringing the mixture to a boiling-point.

The product is usually impure, and a much better one is obtained by heating a mixture of clay and bauxite in a shaft-kiln or electric furnace. It is doubtful whether a rotary kiln is as satisfactory as these other kinds, owing to the high temperature and the duration of heating which are necessary.

The formation of mullite is facilitated by the presence of certain fluxes. Iron is a very desirable constituent, as it acts as a catalytic agent, and also combines with some of the free silica, forming ferro-silicon, which, being

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[1] Cyanite is usually burned at Cone 13 (1380° C.) and sillimanite at Cone 20 (1530° C.), but the figure mentioned in the text is often satisfactory.

heavy, sinks to the bottom of the furnace and is readily removed. Titanium is also useful, as it restrains the combination of the iron with alumina and causes it to act solely upon the free silica present. In the presence of a fluoride such as cryolite, the evolution of the excess of silica is very rapid; the alumina in the cryolite combines with some of the silica, forming mullite.

The presence of felspar also aids the formation of mullite, by dissolving the free silica and facilitating the segregation of the crystals of mullite. It is not, however, a necessary addition, as large crystals may be produced in the absence of felspar, mica, lime or other flux. Under some conditions, fluxes appear to retard the formation of large crystals. The presence of a high percentage of lime retards, or even prevents, the formation of mullite crystals.

Other *accelerators* which increase the rate of conversion into mullite are sodium and calcium aluminates, zeolites, ultramarine, aluminium hydroxide and natrolite (see Eng. Pat. 402,588—1931). (See also p. 147.)

A considerable amount of skill is required in order to produce mullite of good quality from clay and alumina; otherwise a crude and largely amorphous product is obtained, which is very inferior to that obtained by calcining natural cyanite, sillimanite or andalusite. In preparing the artificial product, it is important not to have any free silica present in the vitrified or molten material, or the cold mass may be vitreous and brittle. With a slight excess of alumina the mass becomes microcrystalline and has all the desirable qualities. The proportion of lime must not exceed 1·5 per cent., or it will seriously reduce the refractoriness.

The question as to whether it is cheaper to make mullite synthetically or to use cyanite or similar mineral depends on local conditions. The present trend seems to be in the direction of the synthetic material.

No material should be described as mullite which does not contain a large proportion of true mullite crystals. So to describe materials of similar composition in which little or no conversion into mullite has occurred is misleading and may cause serious trouble.

Fused mullite has a strong tendency to crystallise, but it usually contains some corundum and a material containing an excess of silica which yields more glass than crystals. When fused mullite is chilled by pouring it through a strong blast of air the pellets do not adhere to each other and are readily ground. Mixtures too rich in silica produce adhesive pellets or a stringy mass which cannot be poured. Any alkalies, lime or magnesia tend to increase the proportion of corundum and of glass.

A valuable paper on the properties of fused mullite has been published by H. M. Kraner.[1]

Sillimanite bricks are made either of artificial mullite, prepared as described on p. 386, or of the natural sillimanite, cyanite or andalusite which has been heated sufficiently to convert most of the material into mullite. (Bricks made by casting the electrically fused material usually contain a large proportion of crystalline alumina as well as crystalline mullite.) The calcined material is ground and graded by means of sieves in a similar manner to grog (p. 380). The use of suitable grades is very important for some blocks of complex shape.[2] The particles less than 80-mesh have a great effect on the permeability of the product.

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[1] *J. Amer. Cer. Soc.*, 1938, **21**, 360.

[2] The use of mullite passing 8-mesh but retained on 12-mesh together with mullite passing 100-mesh has been patented (Eng. Pat. 370,864—1929).

Clews and Green[1] found that the hand-made specimens with the lowest porosity (27·8 per cent.) consisted of:

Sillimanite	— 4+ 8	mesh	34	parts
„	— 8+ 20	„	4	„
„	— 20+ 40	„	9	„
„	— 40+ 60	„	7	„
„	— 60+ 80	„	10	„
„	— 80+120	„	12	„
„	—120+200	„	12	„
„	—200	„	12	„
Ball clay			10	„

The binding clay is usually a ball clay or other refractory clay of high binding power, but for semi-sillimanite bricks (p. 390) a fireclay is used. The proportions required depend on the clay; about 10 per cent. of a good ball clay is usually ample, but 40 per cent. or more of fireclay may be used. A complex bond consisting of calcined silica 50 parts, boric acid 30 parts, magnesia 20 parts, magnesium chloride 5 parts was patented in 1927 by R. L. Frink (Eng. Pat. 306,216).

A bond consisting of "silica derived from silicon ethyl ester" by adding water was patented in 1931 (Eng. Pat. 370,151).

The use of phosphoric acid as a bond was patented in 1930 (Eng. Pat. 387,652).

The plasticity and workability of the mixture decrease rapidly with a reduction in the proportion of clay used, so that there is a great tendency to limit the "sillimanite" to 60 per cent. of the mixture. Excellent bricks are made in this country containing 80 per cent., and in Germany large quantities of first-class bricks are made containing 95 per cent. and more of "sillimanite."

When fireclay is used as a bond, the mixture has a smaller proportion of eutectic and a higher refractoriness under load than fireclay bricks or grog bricks, but the mixture of sillimanite and fireclay must be burned at a higher temperature than fireclay bricks if a sufficiently low porosity and a high resistance to chemical action are to be obtained.

Instead of using a binding agent the material may be fused in an electric furnace and poured directly into moulds in the same manner as fused alumina bricks.

The materials are proportioned and mixed with sufficient water and are shaped in presses in the same manner as grog bricks.

The bricks are usually shaped in power presses, and are dried and burned in the same manner as other refractory bricks, as pressing, instead of hand-moulding, greatly reduces the porosity and permeability (see p. 390). Large blocks and some special shapes are made in moulds which are filled by hand, tamped by a pneumatic tool and consolidated on a vibrating table, such as is used for concrete. Highly complex shapes may be made by adding an electrolyte and casting in a vacuum mould.

The *drying* and *burning* are the same as for grog bricks (p. 384).

Adequate burning at 1500° C. or above is essential for the best bricks; when insufficiently burned the bricks tend to swell and crack in use.

Properties.—Bricks made of calcined cyanite, sillimanite or andalusite

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[1] *Trans. Cer. Soc.*, 1937, **36**, 267.

or of artificially prepared mullite have a high refractoriness dependent chiefly on the nature and proportion of the binding agent. The pure mullite has a melting-point of 1850° C. A good quality of commercial " sillimanite " brick made of 80 per cent. " sillimanite " and 20 per cent. of fireclay has a refractoriness equal to Seger Cone 37 (1825° C.) and a refractoriness under a load of 50 lb. per sq. in. corresponding to Cone 28 (1630° C.). Other mullite bricks have a refractoriness between Cones 36 and 40 (1790°–1920° C.); the material of which these are made contains, approximately, 63 per cent. of alumina and 37 per cent. of silica. The bricks have a similar composition, modified by the nature and proportion of the bond. Thus one well-known make of " 80 per cent. sillimanite " bricks contains 58 per cent. of alumina and 37 per cent. of silica. An equally well-known German " sillimanite " brick contains " at least 60 per cent. of alumina " and another contains " more than 70 per cent. of alumina." The best German bricks are said to contain at least 95 per cent. of " sillimanite," have a specific gravity of 2·35–2·42, a refractoriness-under-load of 1620° C. and a porosity of 20–23 per cent.

Pure mullite on prolonged heating above 1550° C. decomposes, corundum being liberated.

Bricks of the sillimanite or mullite type have a very low coefficient of expansion[1]—$2{\cdot}9$–$6{\cdot}6 \times 10^{-6}$ up to 1600° C.—they are resistant to shock by impact, have a mechanical strength when cold greater than fireclay bricks and a higher refractoriness-under-load. They show no change up to 1500° C., and then collapse slowly as the temperature rises to 1750° C. In this they resemble fireclay rather than silica, but are more refractory than fireclay. They are much less sensitive to sudden changes in temperature than are silica and magnesia bricks and are not liable to spall. The thermal conductivity is 0·0035 g. cal./cm./° C./sec.=10·16 B.T.U./sq. ft./hr./° F./in., as compared with 0·0020–0·0025 for fireclay bricks. They have a great resistance to furnace gases and to the materials used in glass-making, but not to some metallurgical slags; they are rapidly corroded by iron-bearing slags and by lime. The presence of 10 per cent. of iron oxide reduces the refractoriness-under-load by 200° C., and 10 per cent. of lime reduces it by 300° C. Up to 1500° C., however, mullite has a good resistance to fluxes. These bricks are very resistant to soda, borax, lime and frits and are, therefore, useful in glass-melting furnaces, in combustion chambers, oil-fired furnaces, boiler-furnaces, rotary cement-kilns, tunnel-kilns, muffles, supports for resistance wires in electric heaters, and pyrometer sheaths. They can be used in furnaces for refining metals and alloys provided no molten metallic oxides come into contact with them. They have proved specially useful in furnaces burning pulverised coal or oil, and generally where a high refractoriness is required in the absence of iron compounds or molten metallic oxides and slags.

" Sillimanite " bricks are not highly resistant to iron oxide, ferruginous slags or molten metallic oxides, though well-made ones, with a refractoriness equal to Seger Cone 37, can often withstand the action of slag better than carborundum or bauxite. The quality of these bricks varies greatly with their composition: mixtures containing less than 50 per cent. of mullite have no greater resistance to the chemical action of alkalies and glass than have fireclay bricks. The durability of " sillimanite " bricks depends also on their texture, which, in turn, depends on the grain-size and the pressure

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[1] Hirsch gives 0·75 per cent. up to 1300° C. For information on the thermal expansion of mullite and similar bricks see Rigby and Green, *Trans. Cer. Soc.*, 1938, **37**, 372.

used in shaping. The specific heat is 0·25. The porosity of pressed bricks is 20–23 per cent.; that of cast blocks is 18–20 per cent. Bricks of still greater porosity can be made. The true specific gravity is 2·8–3·1; the apparent density 2·10–2·40.

One thousand bricks, each 9×4½×3 in., weigh about 4·4 tons. Cast blocks weigh about 145 lb. per cu. ft.

As compared with fireclay, "sillimanite" has the following advantages:—[1]

(i) smaller drying and firing shrinkages;

(ii) greater refractoriness and absence of any tendency to squat when melting glass at 1500° C.;

(iii) capacity to withstand distinctly more rapid temperature changes than prepared fireclay; and

(iv) smaller iron oxide content of the glass melted.

At present the chief drawback to sillimanite as a refractory material is its cost, but the great improvement in the quality of fireclay bricks which is effected by burning the clay under conditions which will lead to the formation of a maximum proportion of sillimanite is so important that they should receive the most careful attention. The cost of making sillimanite bricks is about four times that of fireclay bricks.

Semi-sillimanite Bricks are made of fireclay and one of the calcined minerals of the sillimanite group (p. 147). They usually contain either 40 or 60 per cent. of "sillimanite."

Sillimanite-Alumina Bricks.—According to Chesters and Rees[2] bricks made of 76 per cent. of calcined cyanite and 24 per cent. of alumina calcined at 1650° C., and burned at 1650° C., have no shrinkage and are of excellent texture and resistance.

Bricks made of sillimanite or allied minerals and about 10 per cent. of ball clay have a drying shrinkage of little more than half that of clay alone, and the linear shrinkage of firing is under 1 per cent.

Bricks made of sillimanite and allied minerals appear to be particularly suitable for use in glass-manufacture. They are not resistant to ferruginous slags, particularly under reducing conditions.

Cyanite Bricks are made by mixing calcined cyanite with fireclay or other binder, and as the cyanite is converted by calcination into sillimanite or mullite, cyanite bricks are the same as sillimanite or mullite bricks.

Good *insulating bricks* are claimed to have been made of raw cyanite (28–48) 20, raw cyanite (–100 mesh) 14, plastic bond clay 34, white pine sawdust 12, and water 20 per cent. The bricks were fired to cone 15 (1453° C.) in 25 hours.

The most serious objection to the use of raw cyanite is its excessive expansion on heating, which makes it difficult to produce bricks free from distortion.

CLAY-SILICA BRICKS.

Bricks made of fireclay and ganister or silica rock are known as clay-silica bricks, or more frequently as *semi-silica bricks*.[3] They form an intermediate class between bricks made of clay and those made of silica, and are also analogous to grog bricks, in which the grog has been replaced by silica.

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[1] Cousen and Turner, *J. Soc. Glass Tech.*, 1925, **9**, 334.

[2] *Trans. Cer. Soc.*, 1930, **29**, 306.

[3] For other kinds of semi-silica bricks, see p. 462. Instead of an artificial mixture of clay and silica, a highly siliceous clay may be used.

Clay-silica bricks frequently have a greater resistance to prolonged heating than ordinary fireclay bricks, and they possess a high resistance to crushing (due to the clay present) and great constancy of volume (due to the simultaneous presence of clay—which shrinks—and silica—which expands). They neither shrink, like clay bricks, nor expand, like silica bricks.

The addition of ganister or other form of silica improves the drying power, and produces bricks which will stand sudden changes of temperature better than those made wholly of fireclay.

Many manufacturers prefer to make clay-silica bricks rather than grog bricks, because they do not burn the silica before use, and if sand can be employed, it saves the expense of crushing. Unfortunately, there are very few forms of silica which are really satisfactory for this purpose.

The addition of sand, ganister, or silica rock to a highly refractory clay is, however, accompanied by a serious reduction in the refractoriness of the clay, as mixtures of silica and clay have a lower refractoriness than either silica or clay alone, unless the clay is very impure.

The purer the clay the more serious is the reduction in refractoriness, so that the addition of silica to a highly refractory clay is a misuse of good material. To siliceous clays, on the contrary, the addition of silica may be advantageous, and its effect on the refractoriness may be negligible. This is best understood by studying fig. 29. Mixtures corresponding to the lower part of the curve should be avoided where refractoriness is important.

When some fireclays of inferior refractoriness are mixed with free silica, the heat resistance of the mixture is sometimes greater than that of the clay, so that this forms a convenient method of utilising some fireclays which, alone, would be unsuitable for firebricks.

Bricks made of mixed materials, such as silica and clay, are more readily attacked than those made of fireclay alone, or of clay and grog, as the latter expand or contract uniformly throughout, whereas silica expands, whilst the clay shrinks, and so produces a texture which is more porous than is usually anticipated. It is a curious fact that when clay-silica bricks are attacked by a basic slag, the free silica is scarcely affected, the action of the slag being chiefly on the bonding clay.

Other objections to the addition of silica to clay have already been mentioned in the section on Fireclay Bricks. They apply with equal force to semi-silica bricks.

In clay-silica bricks, the particles of silica are cemented together with a refractory clay. The silica must have the same characteristics as for silica bricks ; the clay should be a binding clay, unless a large proportion of clay is to be used, when a fireclay will probably be satisfactory.

The use of an extremely pure silica is not necessary, provided that the silica used does not melt below 1730° C. (Cone 33). Much more important than its chemical composition, is the behaviour of the silica on repeated heating to 1500° C. (Cone 18). Silica which expands on repeated heating at this temperature is almost useless for refractory work.

The friability of some articles made of a mixture of clay and silica is almost entirely due to the use of silica, which expands on repeated heating. Curiously enough, the purest quartz crystals show this defect the most extensively.

The sizes of the silica particles is important, as fine silica and clay form a more readily fusible material than when coarse silica is used. It is, therefore, important not to have too large a proportion of the finest particles present.

Kraze [1] found that the smaller the particles of silica, the larger the pro-

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[1] *Sprechsaal*, 1908, No. 34.

portion of water required to make a plastic paste, the longer the time required for drying the bricks, the greater the shrinkage in drying, the greater the mechanical strength of the finished bricks, the greater the reaction between the clay and silica, and the greater the sensitiveness to sudden changes in temperature. He also found that with particles of silica of a given size an increase in the proportion of silica reduces the proportion of water required to make a plastic paste, shortens the time required for drying, reduces the shrinkage and porosity of the bricks, and makes them less sensitive to rapid changes in temperature.

The proportion of free silica and clay may be varied within wide limits, according to the properties which the bricks are required to possess, but it is not customary to use more than two parts of silica to each part of clay, and equal parts are satisfactorily employed by several manufacturers.

The proportion of clay and silica should be made to depend on the characteristics which it is desired the bricks should possess. In 1879, New and Thomas patented the use of 4 parts of ground flint and 1 part of fireclay; in 1883, A. H. Dunnachie patented a mixture of silica and fireclay; in 1884, E. Brooke patented a mixture of 90 " parts " of stone, 12 " parts " of fireclay, 3 gallons of tar boiled with a little oil, and 12 gallons of water.

A well-known brand of Belgian firebricks used for coke ovens is made of—

Raw Belgian clay	31 parts
Burned Belgian clay (grog)	52 ,,
Silica	17 ,,
	100

Clay-silica bricks are frequently made in the same manner as silica bricks, as the clay present seldom has sufficient binding power, and lime or other bond must be added to render the manufacture of the bricks possible. When the proportion of clay reaches 25 per cent. or more, semi-silica bricks are preferably made in the same manner as grog bricks, the silica rock being used instead of grog.

The paste of which clay-silica bricks are made is more plastic than that used for silica bricks. It is best prepared by mixing the ground, dry clay and silica together in the desired proportions, then adding enough water to form a stiff, friable paste and mixing thoroughly in a trough mixer. The bricks are hand-moulded in the usual manner, but as the paste is so stiff it must be well beaten after it has been placed in the mould.

Uses.—An advantage of clay-silica bricks is that they will stand a greater load at 1350° C. without deformation than will bricks made wholly of clay. This only applies to bricks in which the expansion of the silica has been completed in the process of manufacture; otherwise, clay-silica bricks are not nearly so strong mechanically as fireclay or grog bricks, because the clay and silica act in opposite directions when heated. Clay-silica bricks are readily attacked by slags and other chemically active substances, so that they can only be used for the upper parts of furnaces; they are particularly useful for arches and crowns and for coke-oven flues on account of their great constancy of volume. They are also useful for the upper parts of cupolas and crucible furnaces, the roofs of round kilns, water-tube-boiler furnaces, the back-walls and roofs of puddling and air furnaces, for the soles of coke ovens and all other work where absence of shrinkage or expansion is an important factor.

Ewell bricks are made from a loamy sand of a greenish-grey to white colour which occurs in deposits up to 5 feet thick at Ewell and Epsom. It is also found at Chalfont St. Peter, Bucks. Their composition is indicated by the following analysis:—

Silica	84·65
Alumina	8·85
Lime	1·90
Magnesia	0·35
Oxide of iron	4·25

They are red in colour, due (no doubt) to the amount of iron present, extremely soft, can be readily sawn or rubbed down to shape, but break easily, and require handling with great care.

Ewell bricks are moderately refractory, but the material of which they are composed is too rich in fluxes for highly refractory bricks to be made from it.

Their chief use is for the cooler parts of domestic fireplaces, furnaces, boiler and retort settings, etc., particularly where the bricks require to be cut to a special shape. They are extensively used in the South of England.

Obsidianite bricks made by Charles Davison & Co., Ltd., are really clay-silica bricks made of a finely ground siliceous fireclay, and are burned so as to form a vitreous glass-like mass which is acid-proof, has an absorption of only 0·31 per cent. and a crushing strength of 5½ tons per square inch. They are chiefly used for packing Glover towers or acid chambers, for which they are quite suitable, being very strong and not too heavy, as each brick weighs less than 4½ lbs.

FLINT CLAY BRICKS.

In the States of Pennsylvania and Ohio, U.S.A., occur highly refractory clays which are almost devoid of plasticity. These so-called "flint clays" do not occur in Great Britain, but in the United States they are extensively used in the manufacture of refractory goods. (Information respecting the composition and nature of these flint clays will be found on p. 139.)

Firebricks are made from flint clays in a manner which is almost identical with that used for grog bricks, the non-plastic flint clay being crushed to particles of suitable sizes, mixed with a binding clay and then made into bricks by hand- or machine-moulding.

The precautions necessary in manufacture are the same as for grog bricks. This applies especially to the grading of the particles of flint clay, the avoidance of an excess of plastic binding clay, and the necessity for thorough mixing.

The best bricks are those made from a hard flint clay or calcined flint clay, with enough bond clay to fill the voids, the mixture being ground very fine, pressed hard, and burned to form a good bond, but not vitrified. Such bricks stand abrasion tests well, and will not crack when subjected to sudden changes of temperature.

According to W. Stout, flint clay firebricks are better when burned in coal-fired kilns than in gas-fired ones, his reason being that each time the fire is fed with fresh coal the bricks cool slightly. This heating and cooling effect causes an annealing or firmer setting of the grains, with consequently a more complete bonding of the mass. Bricks burned in gas-fired kilns are not subjected to this heating and cooling effect, and so are often imperfectly annealed.

The same authority states that flint clay bricks should be burned at Seger Cones 13 to 15. At Cone 13 the water shrinkage is completed, and there is no need to go beyond Cone 15.

PLUMBAGO BRICKS.

As stated on p. 191, graphite, plumbago, or other form of carbon is sometimes added to fireclay bricks in order to increase their conductivity of heat or their resistance to acids or to sudden changes in temperature. The use of fireclay and plumbago for making firebricks was patented in 1879 by W. Hope and R. S. Ripley, in 1880 by S. G. Thomas, and since that time by several others.

In all cases, from 15 to 25 per cent.[1] of plumbago is generally considered to be the most suitable proportion, this material being added to the crushed clay just before the latter is mixed with water. The process of manufacture of plumbago bricks is precisely the same as that for ordinary fireclay bricks, and is very similar to that for crucibles (Chapter XII.). The properties of plumbago bricks are similar to those of ordinary fireclay bricks, but they have a closer texture, show a somewhat greater resistance to corrosive slags and bases, and they allow heat to pass through them more readily. This is a disadvantage in lining furnaces, but is valuable for the partition walls of coke ovens and similar structures.

BRICKS OF CARBONISED CLAY.

Highly refractory bricks may be made by a process patented by W. Smith (Eng. Pat. 149,440), which consists in embedding fireclay bricks in powdered coke or oil-shale, or by impregnating the bricks with liquid or gaseous carbon compounds and burning them without access to air at any suitable temperature between 700° C. and 1600° C.

Such bricks are quite black, and consist of a very intimate mixture of burned clay and finely divided carbon; they are very dense, unaffected by acids, and more resistant to slags than are ordinary firebricks.

When the black carbonised clay is heated under oxidising conditions so that all the carbonaceous matter is burned away, the product is known as "white carbonised clay." It is more porous than ordinary firebricks, but its shrinkage, when in use, is negligibly small.

Both black and white carbonised clay may be used as a highly refractory grog in the manufacture of bricks, crucibles, etc.

ASBESTOS BRICKS AND BLOCKS.

Bricks containing a large proportion of asbestos are light, porous, and good for partitions and other structures where considerable refractoriness is required, but where resistance to slags and other abrasives is not needed. Moulded pieces of this character, especially those of tubular shape, were extensively used at one time as "fuel" in gas stoves for domestic purposes; now, most of these "gas fuels" are made of the same material as grog bricks, care being taken to keep them as porous as possible by the use of plenty of grog or by adding kieselguhr.

Numerous processes have been devised for the manufacture of bricks containing asbestos, but in the majority of these, the asbestos appears to play the part of a filler rather than to be added on account of any intrinsic property. Many such bricks are not refractory, as defined on p. 1, and need not be con-

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[1] The manufacture of firebricks containing more than 30 per cent. of carbon is described in Chapter VI.

sidered here; the following statements relate solely to refractory bricks and blocks in which asbestos is an important constituent.

An early patent for the manufacture of asbestos bricks is that of A. Dudgeon in 1877, in which short-fibre asbestos mixed with silicate or stannate of soda is moulded into bricks, with or without pressure, and then burned. In 1880 H. Bollinger patented the use of asbestos with water-glass or kaolin, the bricks being afterwards impregnated *in vacuo* with a solution of magnesium chloride. In 1889 Beaurain patented, in Germany, the manufacture of bricks composed of 75 per cent. of asbestos and 25 per cent. of fireclay. In Hutcheson and Service's patent (1898), a mixture of 15 per cent. of asbestos and 85 per cent. of fireclay is specified, but is now considered much too rich in clay. Twice as much asbestos as is specified in this patent is much more suitable, and this is the proportion (viz. 1 part of asbestos to 2 parts of fireclay) which was patented by S. O. Cowper-Coles in 1909. For some unexplained reason, the addition of 2 to 10 per cent. of lime is recommended in Cowper-Coles' specification.

The addition of a small percentage of graphite increases the heat conductivity of the material, and, in the case of " gas fuel," it has the advantage of darkening the colour and giving the red-hot material a closer resemblance to a coke fire.

Asbestos bonded with pitch dissolved in benzol is not an attractive material to handle, yet it was patented in 1904 by R. Mueller. A. F. Quin and C. Lacey (U.S. Pat. 1,355,689) patented the use of a mixture of ground mica, asbestos, and salt in the manufacture of firebricks.

The use of a mixture of asbestos fibre, silicate of soda, syrup and borax was patented in 1932 (Eng. Pat. 408,386).

More complex mixtures have been patented, but it is questionable whether they confer any advantages.

Asbestos bricks are not now regarded with the same favour as formerly.

LIGHT-WEIGHT AND INSULATING BRICKS.

A vacuum is the best heat-insulator, but is seldom available in furnaces, kilns, or other highly heated appliances. Only slightly inferior to it is a space containing perfectly motionless air. Such a space may be left between two rows or courses of bricks, or a large number of minute spaces may be included in a highly porous brick or loose mass of material.

For temperature of 500° C. or above, refractory materials, usually in the form of highly porous bricks or slabs, are used, but for lower temperatures, a suitable space may be filled with (i) light magnesium oxide mixed with one-sixth of its volume of long-fibre asbestos, or (ii) slag wool. Alternatively, the magnesium carbonate may be mixed with syrupy magnesium chloride so as to form a paste which can be moulded to any desired shape or applied to existing brickwork as a plaster, though at the sacrifice of some of its insulating power.

The relative insulating powers are approximately—

Vacuum	100
Motionless air	98
Loose magnesium oxide (magnesia levis)	95
Slag wool	90
Loose kieselguhr	75
Highly porous bricks	60–70

The nauseous mixtures of clay and various organic materials usually have an efficiency of less than 40 per cent., and rapidly deteriorate with age.

Light-weight and insulating bricks are of nine varieties:

(*a*) Those made chiefly of diatomaceous earth (kieselguhr, diatomite, moler, etc.). *These bricks* (*i*) *may be cut from the natural mineral* (not moulded) and can then be used up to 870° C.; they are often preferred to other bricks when used below this temperature on account of their greater insulating power, which is about three times that of non-diatomaceous bricks and more than double that of burned diatomaceous bricks; or (ii) they may be mixed with fireclay or other bonding material, pressed or moulded, dried and burned like other bricks. Diatomaceous bricks of satisfactory quality can also be made by compressing the loose powder, previously mixed with clay, in a dry state, but usually they are made by adding clay and using the hand-moulding or extrusion (wire-cut) process.

Light-weight articles are also made from a mixture of kieselguhr and fireclay. The use of such earth with a fireclay bond was patented by C. Hannay in 1897, provision also being made by him for the addition of paper pulp to increase the porosity of the bricks still further. The kieselguhr—washed, if necessary, so as to remove any injurious impurities—is mixed with a suitable quantity of a highly plastic clay—preferably ball clay—water, and, in some cases, with milk-of-lime, either a pug-mill or pan-mill being used. The mixture is then made into blocks or bricks by any convenient method, though hand-moulding is the most suitable, as mechanical pressure reduces the porosity and, therefore, the insulating power of the finished product. The blocks are then dried and fired like fireclay bricks, except that the finishing temperature does not usually exceed 1000° C., though some manufacturers burn such bricks at 1050°–1180° C. (Cone 5*a*). Only the purified, white-burning diatomites can be burned at the higher temperatures; the red ones are too fusible.

In order to ensure a thorough mixing, some manufacturers make the clay into a slip containing an equal weight of water and add this to the diatomaceous earth in a special mill.

Two well-known kinds of American bricks are made of diatomite and cork, with clay as a binding agent.

Bricks made of purified calcined diatomite and fireclay may be used at 980°–1370° C., according to the purity of the materials.

Table LXVII., due to R. H. Horning, shows the relative loss of heat and, therefore, the insulating power of kieselguhr bricks in comparison with those of other materials.

TABLE LXVII.—INSULATING POWER OF VARIOUS BRICKS.

Material.	Weight in lbs. per Cub. ft.	Temperature Difference in °F.													
		200	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500
Magnesia brick	164·0	268	273	276	280	284	288	292	296	300	302	305	307	309	310
Silica brick	97·0	123	127	132	136	139	142	145	148	151	153	154	156	158	159
No. 1 firebrick	131·0	52	57	62	66	70	74	77	81	83	85	86·5	87	87·5	87·5
Repressed, burned Kieselguhr brick	23·2	24	25	26	26	26·5	27	27·5	27·7	28	28·1	28·2	28·5	28·5	28·5
Natural Kieselguhr brick (perpendicular to grain)	33·0	19·9	20	20·5	21	21·5	21·9	22·3	22·7	23·1	23·5	23·9	24·3	24·7	25·2
Nonpareil insulating brick	21·0	13	14·4	15·6	16·8	17·8	18·8	19·6	20·1	20·6	21·0	21·1	21·7	22·0	22·2

Some light-weight bricks appear to undergo less deformation when heated under a load of 50 lbs. per square inch at 1350° C. than ordinary firebricks under the same conditions.

Great care is needed to ensure (i) correct proportioning, (ii) thorough mixing, and (iii) skilful drying and burning, or the bricks will be irregular in their properties. In selecting diatomaceous earth, a microscope is a more reliable guide than a chemical analysis, as the former can show the proportion of actual diatoms and that of other forms of silica.

(*b*) Those made of a mixture of clay and carbonaceous material such as anthracite, coke, peat, lignite, cork, sawdust, seeds, or other combustible material. The latter is burnt away in the kiln, leaving bricks which are very light and porous. The size and shape of the pores depend on the type of combustible material employed. Soft-wood sawdust gives larger pores than hard-wood sawdust. The sawdust must consist of small particles only; larger ones should be removed by screening or by an air separator. The size of the particles may be varied to suit the user; for hand-made blocks they should all pass through a 30-mesh sieve, but for machine-made blocks a 24-mesh sieve will suffice. Hard-wood sawdust is the best, but not easy to obtain in sufficient quantities. Larch- and fir-wood may be used, but pine-wood sawdust is liable to "ball up" if it is at all damp, and cannot then be mixed satisfactorily with the clay. Other carbonaceous material should consist of small particles of nearly spherical shape. It should not be as fine as "dust," but all coarse pieces and fibre should be separated by sieves. The proportion of combustible matter which can be added depends on the binding power of the clay. Some manufacturers use too large a proportion of sawdust and so involve themselves in needless difficulties. Unless the clay is exceptionally suitable, it is better not to add more than 25 per cent. (by volume) of sawdust, though with specially suitable clays as much as 60 per cent. of skilfully graded sawdust may be used, but 40 per cent. is usually the maximum. The more closely the particles of carbonaceous matter resemble small spheres of uniform size the nearer will the maximum porosity approach to 65 per cent. With particles of irregular shape and of different sizes there is no theoretical maximum porosity: the figure then depends on the binding power of the clay. The clay used must have ample binding power or it will not permit the addition of sufficient carbonaceous matter to the clay. Some clays contain too much free silica and may be greatly improved if some of it is removed by a washing process. Some other clays are naturally deficient in binding power. Plasticity and binding power are two distinct properties, and a clay may appear to be very plastic and yet have so little binding power that it is useless for making insulating bricks. If the bricks are not to be used at temperatures above 1100° C., a mixture of ball clay and fireclay will enable a larger proportion of combustible matter to be used than if fireclay were the sole binder. The greater the binding power and refractoriness of the clay, the larger will be the proportion of carbonaceous matter which can be added.

The carbonaceous matter acts as a fuel and necessitates some care in setting. It is seldon wise to fill the kiln completely with these bricks, but to confine them to the upper third of the setting. The bricks may be set fairly closely, but not "tight," as air is required to burn away the carbonaceous matter. Instead of clay and carbonaceous matter, calcined sillimanite 58 parts, anthracite 35 parts, and bentonite 7 parts may be used; with care and skill bricks made of this mixture may have a porosity of 70 per cent. and show only slight subsidence when heated under a light pressure at 1350° C. An accurate proportioning is necessary and the materials should be mixed in the most thorough manner possible. The shaping (whether by extrusion or pressing) calls for no comment, but the burning needs care to prevent overheating whilst burning out the carbon. The fuel used for the kiln should be burned separately, and not in fire-pillars formed by the goods, as is often done with common bricks. If a continuous kiln is used, the firing zone must be longer than for common bricks, as the burning of the carbonaceous matter must be carefully controlled. It is often necessary to cease adding fuel during part of the burning, as otherwise the carbonaceous matter would burn away so rapidly that it would cause distortion in the bricks. When it has burned away, the use of fuel can be continued until the firing is finished.

The later stages of the burning require skilled attention, as the finishing temperature, and that at which distortion occurs, lie very close together, and even a slight overheating may spoil many bricks. It is especially necessary not to allow the temperature to rise too rapidly; the strength of the bricks can be secured with much greater certainty by a prolonged soaking than by a rapid firing at a higher temperature.

Owing to their great porosity, light-weight bricks can usually be cooled very rapidly, and if care is taken the burning and cooling need not exceed 48 hours when suitable clay and wood are used. With some materials, on the contrary, the charred mass formed requires 24 hours or more to burn away, and this slows down the whole of the firing.

The addition of sawdust increases the porosity of the burned bricks by an amount equal to about half the volume of sawdust added. The weight of the bricks is controlled largely by the proportion of sawdust, but the porosity and specific gravity of the burned clay also influence the final porosity of the bricks as a whole. About 4 lbs. appears to be a minimum weight for bricks with good working properties.

There is no relation between the porosity and thermal insulating power of the bricks, and no simple and wholly satisfactory method of comparing the insulating power of different bricks has been found, the methods described on p. 373 requiring much skill, and are not by any means completely satisfactory.

Hot-face insulating bricks are usually made of fireclay and carbonaceous matter, because no variety of diatomaceous earth is sufficiently refractory, but they can be made of a non-plastic mixture (such as sillimanite and anthracite) if a good binding agent is added.[1] Such bricks are used for lining kilns and furnaces, so that they are exposed directly to the flames and hot gases, whereas diatomite bricks must be sheltered behind at least 4½ in. of firebrick. Hot-face insulating bricks are readily attacked by slags, but this is sometimes lessened by coating them with a refractory cement. Experiments are in progress whereby hot-face insulating bricks can be rendered impervious to slag and more resistant to abrasion. If they succeed a great advance in furnace-construction will be possible.

Hot-face insulating bricks have an added advantage because their surfaces, when in use, are hotter than the corresponding surfaces of ordinary firebricks, and this increased glow is of advantage in radiating heat.

Hot-face insulating bricks and other highly porous fireclay bricks may be used up to the safe working temperature of the fireclay, *i.e.* up to 1600° C. if a No. 1 fireclay is used.

(*c*) Those made by adding a frothing agent, such as the root of *Saponaria*

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[1] Pole and Moore, *Bull. Amer. Cer. Soc.*, 1938, **17**, 355, use cyanite, clay, and sawdust.

officinalis or prepared saponin, to fireclay, producing a paste and then blowing in air under pressure, so as to produce a frothy mass which is then moulded, dried and burned. In a method recommended by Khananov[1] a froth is made and mixed with the clay-paste, the mixture being then moulded by hand in zinc-lined boxes, dried for 3–4 hours at 60° C., then completely dried at 100° C., and afterwards fired at 900° C. "Their quality surpassed all other kinds of insulating brick." It is usually necessary to 'fix' the froth by mixing a little alum (in solution) with the clay before adding the froth.

Bricks made of frothed fireclay can be used up to about 1300° C.

(*d*) Those made by adding a gas-producing agent to a clay or clayey mixture. The addition of a small proportion of powdered calcium or some calcium-magnesium alloys to a clay will produce a porous body of very uniform texture. Similarly a mixture of clay, plaster of Paris and dolomite, made into a paste with water and then mixed for two minutes with a suitable quantity of dilute sulphuric acid, will produce a porous mass (Eng. Pat. 411,534). It must be moulded and dried quickly before the gas escapes.

The addition of finely powdered aluminium to a clay-paste containing a little alkali will also produce a porous mass.

The drying of frothed bricks (even when they are made by casting in a plaster mould) is often very uncertain. It appears to be necessary to dry very slowly at a low temperature and only to finish at a higher one. The burning calls for no special comment.

The chief objection to frothed or bloated bricks is their very irregular texture, so that their porosity and other properties usually vary far too much to be satisfactory.

(*e*) Those made by using a material, such as *vermiculite* (p. 13), which expands greatly on heating as the result of the loss of combined water. The vermiculite is mixed with a binder, such as clay, bentonite or sodium silicate, and made into bricks with a highly porous body, which will withstand much higher temperatures than diatomaceous earth. It has no tendency to spall and can be used for very short periods up to 1370° C. and for prolonged heating up to 850° C.

In the preliminary heating, before being made into bricks, the vermiculite expands to twenty times its original volume and so forms a highly porous material of good insulating power. Vermiculite bricks are weaker than cork and have similar heat-insulating properties, but can be used at a bright red heat (below 850° C.).

Aluminium monohydrate, produced in the manufacture of alumina, is of this type. It is very pure, has a low apparent density (45 lb. per cu. ft.) and can be used in the form of bricks up to 1420° C. Its thermal conductivity at high temperatures is about half that of fireclay bricks.

Some *cyanite* (p. 149)[2] swells greatly when heated and can be used for light-weight bricks if previously mixed with 7 per cent. of bentonite and 10 per cent. of ball clay. The porosity is usually increased by adding up to 35 per cent. of anthracite, thus bringing the bricks into class (*b*). Bricks made of cyanite, anthracite and a clay bond can have an apparent porosity of 65–70 per cent.

(*f*) Those made of clays and shales which bloat naturally on heating. These are, unfortunately, useless at high temperatures, as they fuse too readily.

(*g*) Those made of lava, volcanic tufa, pumice, slag wool, or similar materials. These are also unsuitable for use at high temperatures.

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[1] *Stroitel Material*, No. 3, 1936, pp. 18–22.

[2] See footnote on p. 398.

(*h*) Those made by filling hollow fireclay bricks with kieselguhr or other highly porous material (Eng. Pat. 142,955—1919) before or after the hollow bricks [illegible] been fired.

(*i*) Those made by adding a material which volatilises (sublimes) on heating. Naphthalene is the substance most generally used.

Precautions.—The manufacture of light-weight blocks is by no means as easy as is often supposed, much skill being required to produce blocks which are accurate in shape and free from cracks and irregularities.

The high shrinkage of the mixture used produces a complicated burning problem, tends to increase the percentage of breakage, and makes it impossible to obtain an absolutely uniform brick. This, in turn, necessitates the grinding of at least 3 faces of nearly all the bricks produced.

The low mechanical strength of the brick makes it difficult to handle them in the green state and increases green breakage. It also tends to cause excessive bench marks and deformation unless the bricks are burned only one and two deep. Both of these difficulties increase burning costs.

The high percentage of combustible material present complicates the burning operation and makes it necessary to slow up the burning during the time the combustible material is burning out.

Where a volatile substance is used in connection with a combustible, it complicates the drying, making it necessary to recover the volatile material for re-use and also presenting a fire hazard.

The mixtures are usually short and spongy, making it particularly hard to produce dry, pressed or stiff-mud bricks. Most insulating refractories are manufactured by the soft mud process.

Any variation in the moisture-content of the raw materials and the moisture-content of the mix tends to cause considerable variation in the weight per cubic foot of the finished product, as well as in porosity and conductivity.

The sizes of the finished bricks are often irregular and the faces and sides are often so uneven that they would need thick joints. To avoid these disadvantages they may be ground on an abrasive wheel until smooth and of the desired dimensions.

The "loss in dryers and kilns" is often very large. It can be lessened by the addition of about 5 per cent. of water-glass, but this involves a loss of porosity.

The strength may be increased by using washed fireclay or ball clay instead of ordinary fireclay and by mixing the ingredients with unusual thoroughness. The ingredients should be ground and screened separately, or the composition will be irregular.

It is important to determine the thermal conductivity by actual measurement, as some highly porous bricks have very low insulating power, whilst others are too dense to be of service. Samples of diatomaceous earth vary greatly in their insulating power, and this should be tested at regular intervals by those using them. A further cause of loss of insulating power is the overheating of the bricks, whereby some of the pores are filled with fused material. Care must be taken not to submit insulating bricks to greater pressure than they can safely withstand.

Though light-weight bricks are fragile, they can be used under trying conditions (*e.g.* in covers of soaking pits) if reasonable care is taken.

Insulating bricks should not be stored in the open or where they are exposed to damp and frost.

Properties.—Insulating bricks for use at high temperatures should have the following properties :—

(i) Ample insulating power, which is equivalent to a low thermal conductivity (see Tables on p. 403). The usual figure for diatomite bricks is 0·8–2·0 B.T.U./sq. ft./hr./°F./in. and 2·0–9·0 for bricks made of sawdust and clay and for hot-face insulating bricks. The corresponding figures for a good firebrick are 6·5–10 units. A very convenient method for comparing the heat-insulating power of various bricks has been suggested by H. Etherington,[1] as follows:—

A good fireclay brick has a thermal conductivity (k) of 10 B.T.U. per hour per sq. ft. of area per degree F. per inch of thickness of brick at 800° C., and this is taken as the standard. The **standard brick equivalent** for any brick is then found by dividing the figure 10 by the conductivity (k) at any desired temperature. If this calculation is made for fireclay, chrome, magnesite, silica, silicon carbide and diatomite bricks at 1200° C., it will be found that:

1 in. thickness of
fireclay brick =0·9 in. of standard brick
chrome brick =0·85 ,, ,, ,,
magnesite brick =0·40 ,, ,, ,,
silica brick =0·65 ,, ,, ,,
silicon carbide brick=0·12 ,, ,, ,,
diatomite brick =3·1 ,, ,, ,,
diatomite powder =5–25 ,, ,, ,,

Highly porous fireclay bricks of good quality have an equivalent insulating power of about three-fourths of that of good diatomite bricks.

(ii) Constant volume when heated: both expansion and contraction are objectionable, but seldom wholly avoidable. An after-contraction of 0·45 per cent. on reheating to 870° C. is usual with good diatomite bricks, but not more than 0·25 per cent. at 1300° C. should occur with good insulating bricks made of clay.

(iii) Ample refractoriness. Hot-face insulating bricks should be able to withstand the radiant heat, flames and gases to which they are exposed. For such bricks a refractoriness equal to Seger Cone 30–34 is not too high. For bricks which are sheltered behind firebricks a refractoriness as low as that of Cone 6*a*–18 may be sufficient, according to the temperature inside the furnace and the thickness of the intervening bricks.

(iv) The volume-weight should be between 25 and 65 lb. per cu. ft., the lower figure being preferable and 45 lb. taken as a fair average. Some engineers will not use insulating bricks weighing more than 30 lb. per cu. foot, or more than 30 oz. per brick of standard size, except for hot-face work.

Most insulating bricks which weigh more than 60 lb. per cu. ft., or about 3½ lb. per brick, are too dense to be highly insulating and are intermediate between insulating bricks and ordinary firebricks.

The volume-weight of loose purified and calcined kieselguhr is about 0·45, and when slightly compressed it is about 1·3, or 81 lb. per cu. ft., so that diatomite bricks with a smaller volume-weight must usually have been made, in part, of carbonaceous matter.

(v) The porosity should not be less than 60 per cent. and may be as much more as can be obtained without undue loss of strength. The influence of porosity on conductivity is not fully known. The conductivity, up to 500° C., is probably inversely proportional to the porosity, but at higher temperatures and certainly above 1000° C. radiation rapidly gains on conductivity, and the pores, instead of being poor conductors, actually aid radiation.

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[1] *Modern Furnace Technology* (Griffin, 30s.).

The insulating power, when in use, does not depend solely on the amount of porosity, but upon the shape, size and number of the pores, and whether or to what extent they are connected. Small pores have a much greater insulating power than the same total volume of large pores.

(vi) The permeability should be low, as the pores should be separate and not inter-communicating, though some investigations seem to suggest that long needle-shaped interlocking pores are very effective. Contrary to the common belief, the size of pores appears to be of minor importance.

(vii) Freedom from spalling: this is difficult to secure, but with hot-face insulating bricks it should be no less than that of No. 1 grade firebricks, and for the better qualities of diatomite bricks and highly porous clay bricks for use behind a refractory lining it should not be less than that of a No. 2 grade firebrick. According to E. J. Bognar[1] a high alumina-content tends to prevent spalling, but this may only be another way of saying that diatomite tends to cause it.

When insulating bricks tend to spall in use, care should be taken to see that ample allowance is made for expansion; otherwise they may be "pinched" by neighbouring bricks and this may cause the spalling.

(viii) Ample mechanical strength. The maximum usually attainable for bricks made chiefly of diatomite is 800 lb. per sq. in., and 160–400 lb. per sq. in. is usual. Indeed, a crushing strength of 400 lb. per sq. in. appears to be near the maximum attainable with bricks weighing 40 lb. per cu. ft. made by present methods. Bricks made of clay and carbonaceous matter can have a crushing strength up to 2400 lb. per sq. in., but their porosity is then low.

The modulus of rupture is often more important than the crushing strength when cold. It is usually between 150 and 300 lb. per sq. in., being lower with diatomaceous bricks than with those made chiefly of clay.

(ix) The refractoriness-under-load is usually very low. Tests made at 1230° C. and 1320° C. respectively show that only bricks made of clay can bear a load of 10 lb. per sq. in. or more at those temperatures.

(x) The maximum safe temperature of the hot face of the bricks during use depends so much on the bricks that no general figures are really trustworthy. Very few bricks made chiefly of diatomite can safely be used above 950° C. and few bricks made of clay and carbonaceous matter above 1200° C. If the bricks are made of highly refractory clay and nothing has been added to reduce their refractoriness they can be used up to 1550° C. or, in a few cases, 1650° C. without serious risk.

(xi) The resistance to corrosion is low because insulating bricks are all highly porous—this being the property on which their insulating power depends—so that they are readily attacked by slags, dust and other corrosive material.

Bricks made of kieselguhr as well as most 'frothed' bricks must usually be protected by placing a resistant lining of firebricks between them and the interior of the kiln or furnace, but in some furnaces this is not necessary. Where it is desired to use insulating bricks as lining bricks they must be made of fireclay and sawdust; such bricks can be used for what is known as *hot-face* insulation.

(xii) Accurate shape and size are important in order that thin joints can be used. These are best ensured by grinding the finished bricks accurately to size on an abrasive wheel.

Table LXVIII. shows data relating to 13 kinds of American insulating bricks tabulated by G. A. Bole from data by Dr. Rückel.[2]

[1] *Refract. J.*, 1936, p. 78.

[2] *Refract. J.*, 1935, p. 216.

TABLE LXVIII.—PROPERTIES OF AMERICAN INSULATING REFRACTORIES.

Samples.	Refractoriness, Seger Cone.	Permeability.	Conductivity, B.T.U./hr./sq. ft./° F./in.			Load.			Weight, lb. per cu. ft.	Shrinkage, Linear.		Porosity, per cent.	Modulus of Rupture.	Spall Cycle.	Maximum Temp. of Use, °F.
			400° F.	1200° F.	2000° F.	Cold.	2250° F.	2400° F.		2500° F.	2700° F.				
A	34	0·262	2·0	2·8	3·2	158	0·66	3·36	37·7	1·12	1·25	82	91	4	2800
B	..	..	..	..	..	..	4·59	11·02	57·0	..	..	..	..	..	2400
C	32	0·136	1·43	1·91	..	508	11·68	24·07	47·7	6·12	6·90	75	209	10	2200
D	31	0·181	1·19	1·68	..	186	2·57	15·35	38·1	5·20	..	78	101	5	2300
E	32	..	1·68	2·10	2·90	220	..	25·00	41·5	1·25	..	..	170	..	2300
F	23	0·013	1·68	2·00	..	761	3·51	7·02	38·3	2·55	..	79	111	37	2000
G	23	0·089	1·95	2·30	..	276	..	..	37·6	1·33	..	80	89	7	2200
H	34	0·243	1·80	2·40	3·00	102	10·07	22·45	47·0	1·85	4·40	77	162	20	2100
I	31	0·234	2·00	..	3·20	118	24·40	26·50	50·6	2·58	..	76	219	..	2200
J	31	0·173	..	..	..	300	0·0	3·07	54·4	..	5·17	67	182	..	2600
K	28	0·283	1·84	2·25	3·00	579	25·00	..	52·6	1·52	7·00	74	241	2	2200
L	31	0·171	..	..	..	522	0·92	8 78	61·2	2·25	6 00	68	301	13	2400
M	31	0·280	..	..	..	1475	0·00	0·00	39·0	1·00	..	82	300	..	2700

Silocel Super bricks (made by Johns Manville, New York) are claimed to have a higher insulating efficiency than any other insulating bricks which can be used above 1100° C. They have a weight of 2¼ lb. each, corresponding to a volume-weight of 32 lb. per cu. ft., and a crushing strength of 350 lb. per sq. in., or 25 tons per sq. ft. The manufacturers claim that they can be safely used up to 1370° C.

Table LXIX. shows the properties of some English insulating bricks, all made by the same firm for various purposes.

TABLE LXIX.—PROPERTIES OF SOME ENGLISH INSULATING BRICKS.

Hot Face Temp.	Cold Face Temp.	Nonpareil Solid Grade.	Nonpareil Standard.	Newparex Standard.	Newparex High Temp.
° F.	° F.	(k in B.T.U./sq. ft./hr./° F./in.)			
698	86	1·03	0·93	1·54	1·51
1157	86	1·20	1·10	1·80	1·69
1598	86	1·35	1·19	2·00	1·83
Refractory Test,— Seger Cone		10	7	15	32
° F.		2372	2250	2615	3110
° C.		1300	1230	1435	1710
	° F. ° C.				
Shrinkage at (per cent.)	1500 815	nil	0·12	..	..
	1600 870	0·15	0·44	..	..
	1800 980	..	..	..	0·03
	2000 1094	..	..	0·10	..
	2300 1260	..	..	..	0·10
Average density (lb. per cu. ft.)		46	33	41	47½
Average crushing strength (lb. per sq. in.)		400	170	400	560

The differences in some of the chief properties of insulating bricks made by nine English firms are shown in Table LXX.[1]

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[1] J. S. F. Gard, *British Clayworker*, 1937, p. 16.

TABLE LXX.—PROPERTIES OF SOME ENGLISH INSULATING BRICKS.

Brick No.	Density, lb. per cu. ft.	Maximum Safe Temperature, ° C.	Crushing Strength, lb. per sq. in.
A	92·3	1650	Over 700
B	73·5	1094	600
C	41·0	1205	400
D	40·5	1094	500
E	38·8	927	350
F	37·1	900	150
G	33·0	882	195
H	35·2	982	245
I	32·0	871	250 and 100

Hot-face insulating bricks of a well-known make contain 35–40 per cent. of alumina and have the same refractoriness as high-class fireclay bricks (Cone 31). Their conductivity at 1000° C. is only 1·68 B.T.U./sq. ft./hr./in./°F., as compared with 10 B.T.U. for ordinary fireclay bricks, so that the hot-face bricks have six times the insulating power of fireclay bricks. The average weight of bricks 3 in. thick is 2½ lb. (35·5 lb. per cu. ft.). The after-contraction at 1300° C. is 0·1 per cent.

These bricks are much softer than ordinary firebricks and will not resist severe abrasion.

Uses.—Insulating bricks are used for retaining heat in kilns, furnaces and other hot structures and also for preventing heat from entering refrigerators and cold stores. When properly used, insulating bricks can save 10–35 per cent. of the fuel ordinarily used, facilitate the maintenance of a constant temperature when this is required, ensure more rapid heating (resulting in a larger output) and a more even distribution of the heat among the contents of the furnace or kiln. The heating is less influenced by varying atmospheric conditions. The life of the refractory material is increased, as the more uniform heating reduces the risk of spalling and cracking.

The cooling of a well-insulated furnace or kiln should take longer than one which is not insulated, but, usually, the difference is not serious.

The *disadvantages* of the use of insulating bricks are (i) their low resistance to abrasion, corrosion and vibration and (if made of diatomite) their great tendency to spall. For these reasons, insulating bricks should not be subjected to abrasion nor to the corrosive action of flue-dust or slags. Usually they are protected from excessive heat by a layer of firebricks, but this is not necessary with hot-face insulating bricks (see p. 398 and *above*).

Insulating bricks are made in several grades for different purposes. Thus, one firm makes the four following kinds of bricks in various shapes and sizes.

Grade A—insulating brick suitable for a face temperature up to 870° C. and having a crushing strength of 400 lb. per sq. in. Used chiefly in foundations and flues.

Grade B—a standard insulating brick, suitable for a face temperature up to 870° C. and more insulating than A, but with less mechanical strength. Usually employed between a more refractory lining and a stronger structural brick.

Grade C—standard insulating brick, suitable for hot-face temperatures up to 1200° C. Chiefly used between a more refractory lining and an insulating brick of Grade B.

Grade D—high-temperature (hot-face) insulating brick, suitable for a face temperature up to 1350° C. and used as a lining brick exposed directly to the flames and hot gases in the furnace.

The following classification—though not applicable to all bricks or to all uses—is often helpful:—

Group A.—Highly refractory insulating bricks, with a refractoriness equivalent to Seger Cone 30 or above, a weight of 42–60 lbs. per cu. ft., a porosity of 75–85 per cent. and a cold crushing strength of 200–300 lbs. per sq. in.

Group B.—Moderately refractory insulating bricks with a refractoriness equivalent to Seger Cone 20–30, a weight of 27–52 lbs. per cu. ft., a porosity of 70–85 per cent. and a cold crushing strength of 200–500 lbs. per sq. in.

Group C.—Semi-refractory insulating bricks with a refractoriness equivalent to Seger Cone 8–17, a weight of 23–35 lbs. per cu. ft., a porosity of 70–90 per cent. and a cold crushing strength of 200–400 lbs. per sq. in.

Mortar.—It is important to use as mortar an insulating material, or much of the value of insulating bricks will be lost.

Light-weight articles are also made from a mixture of kieselguhr and fireclay. The use of such earth with a fireclay bond was patented by C. Hannay in 1897, provision also being made by him for the addition of paper pulp to still further increase the porosity of the bricks. The kieselguhr—washed if necessary, so as to remove any injurious impurities—is mixed with a suitable quantity of a highly plastic clay—preferably ball clay—water, and, in some cases, with milk of lime, either a pug mill or pan mill being used. The mixture is then made into blocks or bricks by any convenient method, though hand-moulding is the most suitable, as mechanical pressure reduces the porosity and, therefore, the insulating power of the finished product. The blocks are then dried and fired like fireclay bricks, except that the finishing temperature does not usually exceed 1180° C. (Cone 5*a*), and some manufacturers are content to raise such bricks merely to a bright red heat (1000° C.). Only those samples of kieselguhr which when calcined are white or very pale primrose coloured are suitable for use in kilns and furnaces in which a temperature exceeding 1000° C. is attained, as the red-burning varieties are usually too fusible.

Moler bricks are made in a similar manner to other bricks of diatomaceous earth (of which moler is one variety), sawdust or other carbonaceous matter being added, if necessary, to render the product more porous. Some well-made bricks of this kind have a crushing strength of about 1 ton per square inch and a volume-weight equal to (or less than) that of water.

GAS RADIANTS AND ASBESTOS FUEL.

The so-called " asbestos fuel " used for gas stoves now usually consists of porous articles made from a mixture of fireclay and kieselguhr. At one time, a mixture of fireclay and asbestos was used for this purpose, but kieselguhr is now generally preferred.

The materials are made into a stiff paste with water, and each piece of " fuel " is made in two portions in a small hand-press. After moulding, the pieces are stuck together by means of a clay slip, and, when they are sufficiently dry, any imperfectly perforated holes are cleared out with a fine knife.

The pieces of " fuel " are then placed in saggers and burned in a down-draught kiln. It is most important that the pieces should retain a good cream colour, as a poor or irregular colour detracts from their value. Dark spots and " flashings " must especially be avoided.

Usually a finishing temperature of 1100° C. is ample, and for most purposes 1000° C. is sufficient. So long as they are sufficiently strong to withstand ordinary handling, there is no need to impart greater strength by further burning in the kiln.

If white radiants are required, a white-burning clay must be used instead of fireclay, or the pieces may be dipped in or washed over with a white-burning slip.

Mixtures of fireclay and sawdust and of china clay and fireclay are also used. The chief requisite is a porous product which is not excessively brittle and is not sensitive to sudden changes in temperature. It is important that it should be free from cristobalite. Many patents have been granted for mixtures for the production of gas radiants and the backs of gas-stoves. Most of them are of small importance, but it is interesting to note that, for gas-fire backs, Wilson, Turner & Newall, Ltd., have patented a mixture of asbestos fibre 100, borax 5, sodium silicate 75° Tw. 5 parts, with an equal weight of water. The articles are afterwards coated with a refractory wash of pottery clay, fireclay and flour-silica, and are then burned at 1000°–1800° F. (Eng. Pat. 408,386—1932).

CHAPTER III.

SILICA FIREBRICKS.

As their name implies, silica firebricks are composed chiefly of silica, and most of them contain more than 90 per cent. of this material. Among the earliest known silica bricks are those used in four striking panels from the celebrated frieze of archers in the Palace of Darius (500 B.C.), now in the Louvre, Paris. These were shown by Bigot to consist of 90 per cent. of quartzose sand with 10 per cent. of lime. The same authority has expressed the opinion that they were burned at about 1200° C. They absorb 12 per cent. of water, are refractory up to 1750° C., and are readily glazed. Their refractoriness is, however, incidental, as they were used exclusively by the Persians for mural decoration.

Silica firebricks were first manufactured in Europe in 1822 by Young, who made them from the Dinas sand found in the Vale of Neath in Wales, and sold them as *Dinas bricks.* The same gentleman was instrumental in starting the manufacture of ganister bricks in Sheffield in 1858.

Crushed siliceous rocks in other localities were afterwards used, and all the materials mentioned on pp. 165 to 179 have, at one time or another, been employed for this purpose.

For many years, this country had the monopoly of all Europe in the manufacture of refractory materials of this particular class, but as the result of an enormous number of attempts in Switzerland, France, and Germany, there are now several firms on the Continent who, on a commercial scale, produce bricks made of somewhat different forms of silica, but which, nevertheless, possess the main characteristics of Dinas bricks. Indeed, on the Continent, some confusion has arisen from the custom of terming all silica bricks "Dinas bricks," quite apart from their place of origin. This use of the term is unfortunate and should be avoided. Some American manufacturers claim that they are regularly producing silica bricks far superior to any make in Europe, on account of the greater pains taken by them to work accurately to their customers' specifications.

The two essential ingredients of all silica bricks are—[1]

(*a*) *Silica* in the form of a coarse powder. This constitutes nine-tenths or more of the bricks. The various forms of silica which may be used for silica bricks are described on p. 165 *et seq.*

(*b*) *Binding Material.*—As the particles of silica are not plastic and will not unite to form a cohesive mass, the addition of a bond is necessary.

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[1] Apart from the cost of production, bricks made by heating silica in an electric furnace to a semi-molten state and then running it into hot moulds are almost ideal for some purposes. Such a process for smaller articles is described in Chapter XV.

The chief kinds of silica firebricks are—

(*a*) **Silica bricks,** including Dinas bricks, consisting of a siliceous rock, the particles of which are united by a small proportion of bond composed of lime or other base united with silica.

(*b*) **Ganister bricks,** composed almost entirely of ganister or of silica rock to which a little clay has been added as a bond, unless sufficient clay occurs in the natural rock. Ganister bricks are made in the same manner as silica bricks, the differences between them being due to the material and not to the mode of manufacture. The small amount of clay naturally present in ganister reduces the quantity of lime needed to make a bond, though some manufacturers disregard the clay with a view to obtaining a stronger brick. Bricks made of artificial ganister (*i.e.* of a mixture of silica rock and clay) may be made as described under *clay-silica bricks.*

(*c*) **Sand bricks.**—These are only used for positions where an inferior grade of firebrick is satisfactory. They are made in the same manner as silica bricks, lime being used as a bond. The chief disadvantage of sands is the looseness of the particles, owing to the absence of a natural cement.

The use of finely ground waste sand from glass works was patented (1881) by Haddan (later by Pilkington and Ormandy) ; it is only applicable to silica bricks of low grade. Ordinary glass does not form a satisfactory bond, nor is the sand used for grinding and polishing glass a satisfactory material of which to make firebricks, as the grains are too rounded.

(*d*) **Flint bricks,** made of crushed flint, have been the subject of numerous patents, but the heavy shrinkage which flint undergoes when heated to redness makes the use of raw flint undesirable. Calcined flint, on the other hand, was patented in 1881 by Henry Edwards and the Thames Flint Firebrick Co., and attracted some attention in 1916–1918 on account of the short heating period required for the inversion of the silica into tridymite, whereas in bricks made of quartz, even after heating at a higher temperature, the inversion is not complete. Unfortunately, this advantage is accompanied by a very serious drawback (which has been overlooked by several advocates of flint bricks), namely, the ground calcined flint seldom has a sufficiently angular grain to bind well, and the particles are usually too small for the bricks to withstand sudden changes in temperature. The use of flint in high-class silica bricks should, therefore, be confined to the finely ground material which plays so important a part in their manufacture. For this purpose, calcined flint is quite suitable.

In suggestions which have been published for the manufacture of most of the flint bricks, the mode of manufacture is practically the same as for silica bricks with a lime bond.

(*e*) **Porous silica bricks,** made of diatomaceous earth (kieselguhr), are sometimes used for partitions in coke ovens and for the upper parts of furnaces (see " Insulating Bricks ").

(*f*) According to Muir and Hackford (Brit. Pat. 14,934, 1894) the quality of a siliceous material may be improved by mixing it with silicate of soda and firing in such a manner as to produce a *crystalline product.* This is ground, mixed with china clay and silicate of soda, and used for the manufacture of bricks by any of the usual methods. The objection to this process is the use of twice as much bond as usual and the consequent reduction in refractoriness. Apart from this, the use of an artificially crystallised silica is attractive if such a product is obtainable in a sufficiently pure state.

It should be observed that the nature of the siliceous rock creates important differences in the properties of the bricks, and that silica and ganister bricks may, therefore, be divided into the following groups :—

(*a*) *Quartzite bricks*, consisting chiefly of grains of unaltered quartz or quartzite with a bond of glassy material.

(*b*) Bricks composed of a moderate proportion of quartzite grains embedded in a bulky matrix of glassy material and crystals of tridymite.[1] In such bricks about half to one-third of the quartz has been converted into tridymite and cristobalite.

(*c*) *Tridymite bricks*, in which, apart from that in the bond, the silica is wholly in the form of tridymite and cristobalite. These are amongst the most valuable silica bricks, as they are free from expansion and do not spall. Provided that quartzite bricks contain sufficiently small grains of unaltered quartz and a suitable cement, they are often equally good.

It is only right to point out that O. Lange, Endell, and others do not admit that tridymite bricks are of special value, as they have found that silica bricks which have been in prolonged use in a Siemens-Martin steel furnace [2] frequently contain only a small proportion of tridymite. They also consider that tridymite bricks are weaker and have a greater tendency to crack than those made from " unaltered calcined quartz." These investigators agree, however, that bricks made from *findlings-quartzite* and some ganisters, in both of which materials the grains are surrounded by a film of contractile cement, are among the best.

J. H. Sankey & Son, Ltd., of Canning Town, E., claim to have made for some years, though not in large quantities, " silica bricks to any density or specific gravity, that neither expand nor contract, whether during making or in use." They have published the following analysis of their goods :—

Silica	97·41
Alumina	0·67
Oxide of iron	0·40
Magnesia	traces
Potash	traces
Soda	0·81
Loss on ignition	0·17

They have recently used a purer form of silica with excellent results. These bricks are fired at 1600° C., and are exceptionally refractory, as, according to tests made for the makers by Dr Mellor, the bricks show no distortion at Cone 30 (1670° C.) under a load of 50 lbs. per square inch. The makers claim that these bricks contain no free quartz, and that the whole of the silica has been converted into a form stable at high temperatures (presumably tridymite). The porosity of these bricks can be varied within wide limits, and bricks of " one-third less " than the weight of ordinary silica bricks are regularly sold by the firm. Such bricks are not suitable for use under conditions where they are subjected to the action of a blast, to fluxes, or to sudden changes of temperature, but they appear to be of exceptional value where the heat is continuous and the temperature very high.

Uses.—One of the most striking differences between silica and clay firebricks is that the former expand when heated, whilst the latter contract.

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[1] The occurrence of tridymite in silica bricks was first discovered by Mallard in 1880; that of cristobalite by Holmquist some years later.

[2] The variations in the behaviour of silica bricks from different sources, when used in the construction of Siemens-Martin steel furnaces, is very striking. In strong contrast to the observation published in the text are those cases in which the silica bricks have been almost wholly converted into tridymite and cristobalite after the furnace has been charged twelve times.

Hence, silica firebricks are chiefly used where great heat resistance, combined with all absence of shrinkage, is essential. They are, therefore, used extensively in the lining of furnaces, and particularly for the arches, crowns, and higher parts of furnaces and kilns, for the upper parts of glass furnaces, for the hottest parts of gas-fired furnaces and kilns, including reverberatory furnaces, and coke ovens. Indeed, in no branch of industry has the employment of silica bricks spread so rapidly as in the construction of coke ovens, in practically all types of which the structure above the floor level (except the facings) is of silica, while in the recuperative and in some regenerative types its use is extended to that portion of the oven below the floor as well. Fireclay bricks are less suitable for this purpose, as they shrink on heating and tend to fall out after prolonged use. On the other hand, they can stand rapid changes in temperature much more readily than silica bricks, and there will always be engineers who prefer them on account of this quality.

Silica bricks with a clay bond are used where siliceous bricks are required, but need not be so refractory as those with a lime bond, which are more costly to manufacture. Clay-bonded bricks are used in boiler-settings, hardening and annealing furnaces, retort settings, puddling furnaces, etc.

Semi-silica bricks are used where greater constancy of volume is required, as, if properly made of good material, they neither shrink nor swell in use.

Materials.—Although there are many varieties of silica bricks, and some of the most popular of them are sold under various fancy names, they are all composed of compressed silica obtained from various kinds of rocks—principally those mentioned on pp. 165 to 179—the particles being partially cemented together by the addition of bond to the crushed material, and by heating the bricks to such a temperature that they combine with this bond to form a fused silicate which is often of ill-defined composition. In some cases, the rock contains a sufficient proportion of clay or colloidal silica to enable an added bond to be dispensed with (as in the case of the more popular of the various ganisters).

The value of silica for firebricks is determined by the chemical purity, size of grain, and smallness of increase in volume when heated. Too much attention must not, however, be paid to the analysis and refractoriness of the material, as it is by no means unusual to find useless silica rocks which have a high refractoriness (Seger Cone 34) and give, on analysis, results indistinguishable from those of other rocks which are in every way suitable for brick manufacture.

In order to ascertain the value of any rock, other tests must be applied in addition to those mentioned above.

Just as the chemical composition of a silica rock is not, in itself, sufficient as a criterion of its usefulness as a refractory material, so also is little assistance to be obtained from the geological formation in which silica rocks are found. In short, neither the origin, composition, nor refractoriness are the essential factors; what is really necessary is a highly siliceous material composed of sufficiently minute grains united with a cement of amorphous silica. Such a material may be found in almost all the geological formations from Silurian down to recent times.

The raw material must not give too fine a grain when crushed, as that would make the bricks too dense and sensitive to changes in temperature. In order of value for refractory bricks the following materials may be specified: chalcedony, plutonic quartzites, and quartzites from veined quartz. Veined quartz, schistose quartz, sandstones and sand are *not* suitable for making silica bricks; the first two on account of physical structure and the latter two on account of their variability in composition and the fine grains produced from them. The rocks from which all the better qualities of silica bricks are made are those quartzites or metamorphosed sandstones known as ganister, quartzite, and silica rock.

It is important not to use too pure a silica, the best results being usually obtained with rocks containing 97 per cent. of silica and rather less than 3 per cent. of impurities, including 1 to 1½ per cent. of iron oxides.

Old silica bricks are sometimes used with fresh material, but twice-burned silica bricks have a weak inner reactivity and so are poor tridymite-formers. On the other hand, they have a good resistance to slags and so form a useful kind of " grog." If, however, a large proportion is used, the new bricks will probably be brittle and will crack during burning. This is attributed to the existence of two or more forms of silica in the bricks.

The physical condition of the crushed material is also of importance. Rounded grains cannot be used, as they will not bond properly. Even sharp-grained silica is not good if the size of grain is too uniform. A rock which grinds to splinters and particles of irregular size, which overlap and interlock, makes a brick of the best structure. Ganister is excellent in this respect.

The relative value of different samples of siliceous material for the manufacture of silica bricks may be roughly estimated by heating a portion of the silica rock[1] for 4 to 5 hours at 1600° C. to 1700° C. To be of value, the sample should remain intact without loss of shape, but a few small cracks may be disregarded. If the sample cracks and breaks into pieces of considerable size, it will probably be suitable for the manufacture of silica bricks, but if it is disintegrated into very small pieces, it should be discarded. A useful material may sometimes be obtained by calcining flint or a silica rock and rejecting the smaller pieces, but this method is often risky. When tested in this manner, most quartzites and ferruginous sandstones remain compact, as do flints and chalcedony, but pure quartz, many white or grey sandstones, and banded flints fall to powder on account of the strains set up in the crystals and released when the crystals are heated.

The expansion of a silica rock after heating to a temperature of 1700° C. also shows, roughly, the value of the material. Coarse quartzites show an expansion of 9 to 15 per cent., and large crystals crack or disintegrate when heated, producing friable or weak bricks, and are unsuitable for the manufacture of silica bricks unless they are ground very fine. Very small crystals uniformly distributed in a suitable cement or ground-mass are less harmful, and can often be made into good bricks. Chalcedony and argillaceous silica materials have a much lower expansion than quartzites—usually 4 to 7 per cent. —and are, therefore, of greater value.

In apparent contradiction to the foregoing, Le Chatelier has stated that any quartz or quartzite, if sufficiently free from fluxes, can be used for making good silica bricks, provided it is ground sufficiently fine, but the cost of this treatment is usually prohibitive in districts where materials are available which do not need so much grinding.

The value of a silica rock as a refractory material may also be judged from an examination of it under the microscope with a magnification of about 45 diameters, using polarised light, as the useful quartzites contain minute crystals in a glassy ground-mass whilst the useless ones consist almost wholly of larger crystals or sharply defined fragments of such crystals. K. Endell has pointed out that useful quartzites, under these conditions, also have a

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[1] This was the method originally used in some of the steel works in South Wales for distinguishing useful from useless silica rocks for lining furnaces.

uniform extinction over the whole surface of the individual crystals, whereas useless ones are not extinguished uniformly, but in the form of a wave which moves across the surface of each crystal, on account of some of the crystals being distorted by the pressure applied in or since their formation. When a piece of silica rock is seen under the microscope to consist of minute crystals each surrounded by an amorphous coating of silica, the material may usually be employed for the manufacture of silica bricks, as the contraction of this covering of cement neutralises the expansion of the quartz grains.

Silica bricks used for the arches of electric and other metallurgical furnaces should be made of fine quartzites, whilst for glass-melting furnaces, where the temperature is not so high, silica bricks made from coarser Coal Measure quartzites are quite satisfactory, and are not likely to spoil the glass if portions of the bricks fall into it from the crown of the furnace. Coal Measure quartzites may also be used for the silica bricks employed in regenerators, coke ovens, etc. The coarsely crystalline quartzites are only suitable for low-grade silica bricks used in annealing furnaces (see " Preliminary Calcination," p. 422).

Bonds.—As crushed silica—other than some ganisters—cannot alone be made into bricks, it is usually necessary to add a small proportion of some suitable binding material.

The following are the most important bonds used in the manufacture of silica bricks :—

(i) *Lime.*—This is usually employed in the form of slaked lime, stirred with water to form a milk or slurry, and known as *milk of lime*; but ground lime or other calcium compounds may be employed. As quicklime which has been stored for some time absorbs carbon dioxide from the air and so loses some of its usefulness, it is important to employ fresh lime. For this reason, it should be obtained from a near-by lime works, or the stone should be burned at the brickworks—a process which is by no means difficult and has the advantage of ensuring the quality of the lime.

The lime, which must be of good quality, containing not more than 3 per cent. of magnesia, is carefully slaked by hand or, preferably, in a hydrating drum, or it may be purchased as " hydrated lime." The hydrating drum consists of a horizontal cylinder which can be rotated as required. It is provided with rotary blades driven by a belt and pulley. A charge of lime is put into the drum, the requisite quantity of water or steam is slowly added, and the blades rapidly effect the slaking of the lime. The drum is then turned over and its contents are discharged on to a flat sieve with 30 holes per linear inch. The bulk of the lime falls through into a tank below, and if the sieve is rapped or shaken a little, all except the coarse particles will pass through it. The residue on the sieve consists of unslaked lime, etc. It may be returned to the drum for further treatment, or may be thrown aside if it consists entirely of imperfectly burned lime and " impurities." To the hydrated lime a sufficient quantity of water is then added, in order to form a milky-white slurry, and this is well stirred by a hand-beater or by means of mechanically driven blades.

It is convenient to have three sets of tanks—one to contain the material ready for use, one in which the material is being stirred, and the third ready to be filled with fresh lime. This provides ample time for the solution of the lime—an important factor in successful manufacture. It is a mistake to throw lump lime into water, stir well, and then to use this mixture within a few minutes of its preparation. The lump lime should either be hydrated to powder as described above, or it should be reduced to a putty ; on no account should enough water be added to " drown " it, or the production of a good milk of lime will be excessively slow. When the slaked or hydrated lime has been placed in water, it should be allowed to stand for at least twelve hours, preferably in a covered vessel.

Some manufacturers prefer to mix the crudely slaked lime and water in a blunger (fig. 94). This should be well galvanised or else made of wood, as iron and steel are rapidly corroded by lime-water. Any simple form of blunger may be used, provided it has a to-and-fro motion or a suitable set of baffles; the elaborate lime-mixing machines used in sewage works, etc., are neither desirable nor necessary.

When ready for use, the milk of lime should be stirred and passed through a sieve with 50 holes per running inch into another tank, where its strength or content of lime should be tested. This is readily done by measuring out 10 c.c. of the "milk" into a glass or beaker, adding a few drops of phenolphthalein solution, and then running in standard acid drop by drop from a burette until the milk becomes colourless. The volume of acid used will indicate the amount of lime present. Standard $\frac{N}{1}$ acid[1] is of such a strength that 1 c.c. of it corresponds exactly to 0·028 gram of lime (CaO), so that, using 10 c.c. of milk of lime, each c.c. of acid corresponds to 0 028 lb. lime per gallon of milk. By testing in this manner, it is easy to calculate how much lime to add to the silica to produce the required percentage of lime in the bricks.

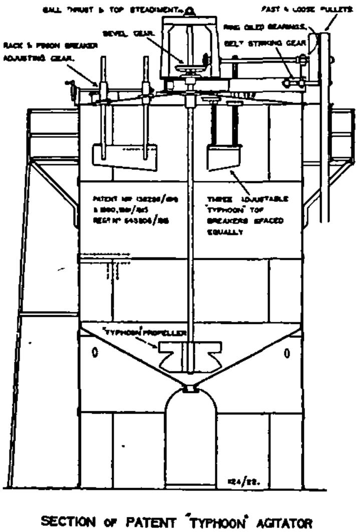

FIG. 94.—Blunger for mixing lime and water.

Some brickmakers omit the sifting of the lime and do not test the milk.[2] This is a mistake, and leads to irregularities in the quality of the bricks.

The use of lime of a low grade is a great mistake in the manufacture of silica bricks. In the first place, it does not prove cheaper in the long run, and, in the second place, its use involves risks which it is always desirable to avoid. Low-grade lime slakes badly; it is liable to introduce fluxes into the mixture used for brick-making, and it tends to make the bricks low in lime. On the other hand, if "enough" of such lime is added to ensure the bricks being sufficiently strong, there is great probability (unless the testing of the strength of the milk of lime is very conscientiously performed) of an excess of lime being added occasionally; this will result in bricks which collapse at too low a temperature.

The proportion of lime required is usually 2 per cent. of the silica,[3] but with some rocks it is necessary to allow the milk of lime to settle before use, so as to obtain a very weak solution, for the rocks themselves, in such cases, contain nearly sufficient lime, and only need the addition of a very small proportion,

[1] Standard hydrochloric acid can be purchased from most manufacturing chemists at about 4s. per quart. It must not be confused with commercial acid, which is of an entirely different strength. Even more convenient are the tubes of "Fixanal" (sold by J. Sherman & Co., Ltd., Downham Mills, Tottenham, London, N. 17), which enable the user to make up a standard solution in a few minutes.

[2] The use of a hydrometer is *not* satisfactory.

[3] If the lime is exceedingly finely divided, 1 to $1\frac{1}{2}$ per cent. will usually suffice.

along with the water required to make the material slightly plastic. The addition of 1½ to 2 per cent. of concentrated wood cellulose lye is stated in H. Spatz's (1904) patent to reduce the amount of lime required to 0·7 per cent. of the bricks, and greatly to increase the plasticity of the paste used for moulding.

The effect of an increase in lime from 2 to 3 per cent. is not marked, but in so far as it can be recognised, it renders the brick less able to withstand abrasion, as shown by rattler tests. The decrease in strength and refractoriness with higher percentages of lime (up to 7 per cent.) is progressive, and becomes more and more evident with each increase. When only 1 per cent. of lime is used, there is a decrease in strength below the normal, and a marked weakness and friability if the amount of lime is still further diminished.

To increase the strength of silica bricks, many German manufacturers add clay as well as lime to form the bond, both these materials being added to the charge in the tempering mill. The amount of clay varies, as little as 5 per cent. and as much as 30 per cent. being used. The manufacture is described under " Simi-silica Bricks."

Slaked lime, mixed with nine times its weight of ganister, is specified in C. Bramhall's patent (1885). The use of slaked lime from magnesium limestone was patented as a bond for silica bricks in 1882 by S. Pitt.

Quicklime, mixed with seven times its weight of silica and one-quarter of its weight of fireclay, is directed to be mixed with sufficient water to form a paste in W. Wilson's patent (1908).

The use of a bond of lime 1, clay 5–6 and quartz 12 parts, all ground to pass through a 200-mesh sieve, was patented in 1932 (Eng. Pat. 382,913).

Magnesia may be used instead of lime, but has never become popular (see Eng. Pat. 4433—1903).

Dolomitic lime was used by S. Pitt in 1882 in the manufacture of silica bricks. On account of the magnesia present, it gives a tough viscous mass when melted, whilst lime gives a thin and very fluid slag under the same conditions.

Chalk is converted into lime when heated to bright redness, and its use as a bond has, therefore, been patented by E. R. Salway, and independently in the same year (1883) by H. Edwards. One part of *chalk marl* (a natural mixture of clay and chalk) to three or four parts of silica is specified in the patent granted to A. W. Fludder and G. H. Innes in 1896.

Portland cement is formed by heating lime and clay to incipient fusion, and grinding the resultant clinker to an extremely fine powder. It has been specified as a bond for silica bricks in several patents, notably those granted (*a*) to S. J. Payne in 1881 for the use of a mixture of 7 lbs. of crushed silica, 1 lb. of Portland cement, and ½ pint of silicate of soda of sp. gr. 1·200—in a later (1886) patent, Payne omits the silicate of soda; (*b*) to H. Edwards and H. Haines, in which crushed silica is moistened with lime water, and Portland cement then added, the proportions being equivalent to 1 per cent. of lime and 2½ per cent. of cement in the finished bricks.

(ii) *Clay* is largely used as a bond, though this is often done unwittingly. In other words, ganister is equivalent to a mixture of silica with about 10 per cent. of clay. Artificial ganisters are, therefore, made by adding clay to the crushed rock. In some cases, clay-bonded bricks are better than lime-bonded ones, but as the former require to be burned at a higher temperature than the latter, lime bonds are usually preferred by manufacturers. If the fireclay is boiled with water and then passed through a sieve with 80 holes per linear inch—so as to separate the useless inert material—it makes an excellent

" natural cement " for silica rocks deficient in such material. If a plastic fireclay is used, 3 per cent. is generally ample for this purpose. G. W. Mottram has suggested the addition (Eng. Pat. 123,116, 1917) of peat water, or the slime deposited from the effluent from sewage purification, or the refuse liquid from tanneries, to the clay used as a binder. Where large quantities of clay are added, semi-silica bricks are produced. The main advantage of adding clay is that the raw bricks are able to withstand much rougher handling, though the strength when burned is not appreciably improved.

Hugill and Rees[1] found that bricks made of calcined ganister and 7 per cent. of ball clay with 0·2 per cent. of sodium silicate (to deflocculate the clay) are more durable than ordinary silica firebricks, especially for electric furnaces and for the doors and arches of basic-steel furnaces, as they are less sensitive to sudden changes in temperature and are less readily attacked by basic slag. They are not, however, suitable for general use in basic furnaces.

When making clay-bonded silica bricks, it is advisable to suspend the clay in water with the aid of a little water-glass and to add the resulting slip to the silica. This ensures a much better distribution than when dry clay is mixed with the silica.

(iii) *Soda compounds* (including water-glass) are occasionally used as bonds. They serve the same purpose as lime, but they produce more fusible bricks. The proportions are usually equivalent to 2 parts of soda (Na_2O) for 100 parts of silica. A mixture of 2 parts of caustic soda, 8 parts of milk of lime, and 90 parts of silica was patented by H. A. D. Collins in 1902; a very similar mixture of equal parts of soda and lime, with twenty-four times its weight of silica, was patented by J. Campbell in 1912, and the use of caustic soda alone, or of soda ash, is specifically claimed in H. A. D. Collins' 1906 patent.

Water-glass (sodium silicate solution) was first patented as a bond for silica bricks in 1878 by S. G. Thomas, since which date it has been patented as a bond for many non-plastic materials. The amount of sodium silicate in the fluid water-glass varies greatly; only a rough idea of it is obtained from the specific gravity of the liquid, as the composition of the silicate varies in supplies from different works. In 1906, H. A. D. Collins patented the use of either an unusually dense water-glass (sp. gr. 1·875), or the rock silicate made by evaporating the fluid to dryness. He made the mixture of silica and bond sufficiently plastic by the use of steam or hot water, which was thoroughly incorporated with the other ingredients. In 1909, I. Schlossberg obtained a patent in which bricks or other articles are made of silica bonded with water-glass and are afterwards saturated with fluosilicic acid and heated to 900° C. to remove the silicon fluoride and form sodium silicofluoride.

In 1914, W. W. Crawford patented the use of a mixture of a silica-clinker with 15 per cent. of its weight of tungstic oxide and sufficient water-glass to make a paste. " The clinker is made by mixing finely divided silica with one quarter of its weight of the refuse from mineral oil stills and calcining the mixture at 2000° C. in a reducing atmosphere until the mass clinkers."

Water-glass does not produce a good bond until it is heated to 500° C.; below this temperature it hardens too slowly to be of much use in the small proportions in which it can be used in firebricks. In the earlier stages of burning it is excellent, but the bricks in which it is used have a lower melting-point than those made with lime; as this is characteristic of the use of water-glass, it cannot be avoided so long as this bond is employed. For second-grade bricks, water-glass may be recommended, but, for the reason given, it

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[1] *Trans. Cer. Soc.*, 1929, **28**, 221–251; 1931, **30**, 373.

is not suitable in bricks which are required to have the highest possible heat resistance.

(iv) *Ammonium alum* has been added very successfully as a bond in the proportion of about 5 per cent. of the weight of the silica. It is readily soluble in water, and is easily applied. *Potash alum* is less satisfactory, for although the alumina in it is considered to add to the refractoriness of the bricks and so neutralise the action of the potash, it does not really do so. The alum is dissolved in water, and is added in the same manner as milk of lime, no difference being made in the mode of manufacture of the bricks. Tests made of bricks from different works in which alum is used differ greatly, and show that much improvement might be made in some cases by a further study of the subject; in some works the use of alum has been highly successful, whilst in others it has been a failure.

(v) *Aluminium sulphate* (patented by G. C. Fludder in 1909) has the advantage over alum—see (iv)—of being free from alkali, but, in spite of its obvious advantages, its use has never become popular. It is soluble in water, and has the same general properties as the alums, but does not exert so powerful a fluxing action on the silica. The hot solution of the sulphate is mixed with the silica in a trough mixer or pan mill. Where very hard bricks or blocks are required, the patentee recommends the addition of ground magnesium silicate—see (viii)—previous to the aluminium sulphate.

According to Sosman [1] alumina and compounds which form it on heating are not desirable as they reduce the miscibility of silica and other oxides.

(vi) *Calcium chloride*, being far more soluble than lime, has been used as a bond with some success. Its use in association with water-glass (2 parts of the former to 5 parts of the latter for each 100 parts of silica) was patented in 1902 by H. A. D. Collins, but the use of calcium chloride alone was patented by H. Brearley and F. C. Moorwood in 1908, the two latter afterwards preferring magnesium chloride (vii). It behaves in a precisely similar manner to lime so far as its bonding power is concerned, but it dissolves perfectly in cold water, so that a clear solution of it can be used, and has the further advantage of forming ferric chloride with the iron compounds present in the silica; ferric chloride is readily volatilised when the bricks are burned, thus reducing the iron-content of the bricks. Unfortunately, calcium chloride has one disadvantage—it is so highly hygroscopic that it is difficult to dry the bricks when used, and the floors must be made much hotter than usual, or the bricks will be sticky and weak in the kiln. If once they are dried, however, and put direct into the kiln before they have had time to absorb any appreciable amount of water, they will stand well enough in burning. During the burning the chloride decomposes, leaving free lime which rapidly attacks the silica, and makes a bond which is better than when milk of lime is used, as the soluble bond is better distributed. One reason for this is because the chloride produces much smaller particles of bond, and has itself a specially strong action on silica, converting it into a soluble silicate at a dull red heat, *i.e.* at a temperature far below the melting-point of the product.

The objection to all chlorides lies in their tendency to scum and to pass to the outside of the bricks instead of remaining uniformly distributed throughout the mass. The expulsion of hydrochloric acid from the surface of the goods when in the kiln is also an objectionable feature of the use of chlorides as bonds.

(vii) *Magnesia* (patented by S. Pitt in 1882, by Williams and Tomkins and independently by E. Stoeffler in 1904), *magnesium chloride* (patented by

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[1] *Blast-furnaces Steel Plant*, 1929, **17**, 1076.

Brearley and Moorwood in 1909), *magnesium silicate*, prepared from waterglass and caustic magnesia (patented by Parry and Cobley in 1880), and other compounds containing magnesium, act in a manner very similar to calcium chloride, but magnesia forms more viscous silicates and therefore makes tougher bricks. The characteristic of all magnesium compounds when heated with silica or clay is that they form silicates or alumino-silicates, which are so viscous that they do not flow readily, and for this reason bricks bonded with magnesium compounds do not collapse so quickly under a load at high temperatures as when the more fluid silicates of lime and alkalies are used. Brearley and Moorwood specify 3 per cent. of magnesia, or its equivalent, as the maximum permissible in a silica brick. It is obvious that a mixture of hydrochloric acid and magnesia, or magnesite, may be substituted for the chloride if desired. For objections to the use of chlorides see (vi).

(viii) *Complex silicates* of various kinds, including *Cornish stone* (patented by E. Robins in 1877), *magnesium silicate* (patented by G. C. Fludder in 1909), have been used as bonds, but no satisfactory details of the results obtained with them have been published. Some of these may be included in section xv.

The use of *felspar* has been tried, but as 10 per cent. of it must be used to produce sound bricks, it unduly reduces the refractoriness of the silica, and so is unsuitable for the better qualities of bricks.

The use of *Cornish stone*, which may be regarded as a mixture of felspar and quartz, is even less suitable for the same reason.

(ix) *Sulphuric acid* is not a satisfactory bond. In the presence of lime it forms plaster of Paris.

(x) *Plaster of Paris* is occasionally used as a bond.. During the earlier stages it is slightly stronger than lime, but, on burning, it behaves just like lime, with the disadvantage that sulphuric acid is evolved and is sometimes detrimental to the bricks. Plaster of Paris acts best if used in conjunction with aluminium sulphate or ammonia alum, though some manufacturers find that these materials are equally satisfactory if no plaster is present.

(xi) *Heavy spar* (barium sulphate) has been used as a bond with moderate success. Its effect is to produce rather more fusible bricks than those made with lime, so that the latter is generally preferable. According to J. Davenport's (1887) patent, about 10 per cent. of barium sulphate is required.

(xii) *Colloidal silica* and *gelatinous silica* have received a considerable amount of attention during recent years, especially since the microscopical examination of various natural silicate rocks has shown that the particles in these are united by silica. The use of gelatinous silica as a bond for silica bricks was patented by C. V. Boys in 1889, and by A. Poulson in 1909; the latter prepared it by mixing silicate of soda of a density of 1·125 with hydrochloric acid of sp. gr. 1·075 and allowing the gelatinous silica to settle. In 1912, Schwerin patented the use of colloidal silica prepared by mixing finely ground silica with a dilute solution of alkali and dialysing the liquid. In 1913 I. Schlossberg patented the use of a mixture of 2 parts of colloidal silica, 93 parts of silica, and 4 parts of lime, the excess of lime being removed from the finished bricks by treatment with hydrochloric acid, followed by a thorough washing. H. Koppers, in 1921, patented the use of a refractory volcanic deposit, occurring in the Eifel Mountains, containing over 90 per cent. of silica (a considerable proportion being colloidal) as a bond for silica bricks.

(xiii) *Iron oxide* is an excellent bond for silica bricks, especially if it is in the form of a highly ferruginous clay. For some purposes, silica rocks which contain 3 to 8 per cent. of iron oxide are quite suitable for the manufacture of silica bricks, the iron oxide combining with the silica and forming a fusible slag which binds the particles of silica securely together. Various waste materials containing iron oxide as their chief constituent have also been suggested as bonds. F. H. Brooke and T. Twynam in 1918 patented the use of ½ to 3 per cent. of fine flue-dust (containing a high percentage of magnetic oxide of iron) obtained from the downcomers of blast furnaces as a bond. Some users of silica bricks will not purchase those in which iron is the chief bonding agent, on account of their dark colour. During recent years the production of *Black Dinas bricks* has increased largely in some parts of the Continent, chiefly because it has been found that the incorporation of 2 per cent. of ferric oxide in a finely divided state ensures the almost complete tridymitisation of the quartz.

(xiv) *Carborundum* as a bond for silica or other refractory bricks has been patented by I. Imray (Eng. Pat. 3308, 1903). It should be in a finely powdered form, and may be used in proportions up to 50 per cent. of the silica-carborundum mixture.

(xv) *Other mineral bonds* of various kinds have been used with varying success. Some of the best of these are excellent, but the conditions under which protection is afforded by the Patent Acts are such that the owners or discoverers of such bonds feel that they must necessarily keep their composition as secret as possible. To publish the information in the form of a Patent Specification results, in many cases, in other manufacturers producing bricks and other goods by the same process, or by the use of a special bond, without in any way recompensing the owner of the patent. For obvious reasons, the author does not intend to publish the composition of the various secret bonds used by his clients, or of which he has obtained information in other legitimate ways, but, as an example of what may be done by careful and assiduous research, the work of G. Cannan Fludder may be cited in this connection. Fludder set out to discover " a bond which was soluble in water, and so acts as an agglutinant and as a suspensory medium for another simple substance which will act as an agglomerant or sintering agent without unduly reducing the refractoriness of the bricks." After considerable research he found several substances which fulfilled these requirements, the substances being varied according as the material to be bonded is acid (as silica) or basic (as magnesia) or neutral (as chromite). The result is twofold: the bricks are much stronger during the earlier stages of manufacture on account of the agglutinant used, and the burned bricks, whilst as strong as those made with the better-known bonds, are more durable and do not collapse so readily when in use. The agglutinant acts with or without the aid of heat, other than that used for drying, but the agglomerant remains inert until the goods are raised to a temperature of about 1500° C., when both it and the agglutinant enter into chemical combination with the material forming the aggregate, and vitrify into a tough and viscous mass, with a negligible amount of corrosion or reduction in the fusibility of the goods. In contrast to the use of lime, which forms a thin and very fusible silicate and facilitates the collapse of the goods if the heating is prolonged, Fludder's bond scarcely affects the squatting temperature of the material, and, whilst lime enters into active combination with the aggregate at a very rapid rate and a relatively low temperature, Fludder's bond acts with extreme slowness, and appears only to combine with just enough of the aggregate to enable a sufficiently strong union of the bond and aggregate to be effected. This slowness of action necessitates a high temperature being employed in burning the bricks, a practice which the author has recommended on other grounds as highly desirable in the case of all refractory materials.

The following tests of bricks made in the same manner as ordinary silica bricks, but using the special bond recommended by Fludder, are particularly interesting and instructive :—

A silica rock containing 2·3 per cent. of lime, potash, and soda, when made into bricks by Fludder's process, showed, when tested by J. W. Mellor, a reduction in refractoriness of only 10° C. to 15° C. from that of the raw rock.

A Durham ganister, consisting of

Silica	97·2 per cent.
Alumina	1·5 ,,
Iron oxide	0·5 ,,
Lime	0·3 ,,
Potash	0·5 ,,

was made into bricks by the Fludder process, and these bricks, tested at the National Physical Laboratory, showed no signs of softening at 1800° C., but thin sections, when supported only at the edges and weighted at the centre, bent under a moderate load at 1850° C. to 1900° C.

Actual tests in steel furnaces confirm the high refractoriness and durability of bricks made in this manner, and supplementary tests in kilns, gas-retort settings and other furnaces, all indicate that the bond used is of ample strength and that the bricks have a toughness and durability markedly greater than those in which a lime bond is used. The expansion of the bricks is dependent on the aggregate used; in the case of the bricks previously mentioned, Mellor found the total expansion as low as 0·16 per cent. at a temperature as high as 1350° C. By using a bond which is not rapid in its action, bricks made by Fludder's process are rendered peculiarly insensitive to sudden changes in temperature, and have been placed directly into a hot fire and then withdrawn and partly immersed in cold water without cracking or shattering them.

By retaining the general principle, but altering the composition of the agglutinant and agglomerant to suit the aggregate, Fludder has succeeded in making bricks of aluminous materials such as bauxite and corundum (Chapter V.), basic materials such as magnesia (Chapter IV.), and neutral materials such as chromite (Chapter VII.), of exceptionally high refractoriness and durability.

(xvi) *Calcium phosphate* as a bond is specified in Eng. Pat. 443,865 (1934).

(xvii) *Temporary* or *organic bonds* are chiefly of use in facilitating the moulding of the bricks, and to ensure the strength of the bricks during drying and setting before the lime has begun to act. Such organic substances burn away at a dull red heat, but are of great value during the earlier stages of manufacture in enabling the bricks to be handled readily with little risk of damage.[1]

Waste products of various industries are usually employed for this purpose, one of the most suitable substances being the sulphite lye obtained in paper manufacture.

Other important ones are—

(*a*) *Tar* (patented by Evans and Tucker in 1881), or *Pitch* (patented by the Swedish Nitric Syndicate (Eng. Pat. 10,591, 1909), which necessitate the materials being worked hot like carbon bricks (Chapter VI.).

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[1] The following organic binders are mentioned in Eng. Pat. 196,021 (1921): dextrin, amylaceous materials, albuminoids, glucosides, glucoses, gelatins, sulphited liquors or residues, resin and asphalt.

(*b*) *Viscous mucilage* (patented by E. Robins in 1877), but commonly replaced by dextrin, flour or starch paste when a temporary bond of this character is desired.

(*c*) *Heavy mineral oils* (patented by J. Williams in 1883).

(*d*) *Cellulose* or cellulose lye (the former patented by Dixon and Reynolds in 1886, and the latter by H. Spatz in 1904).[1]

(*e*) *Sugar* or molasses (patented by G. Palin in 1889).

(*f*) *Various glutinous mixtures* are used. One of these, *plasticade*, a commercial product containing tannin and lignin, increases the strength, reduces the water of plasticity, the pore-water and the shrinkage; as little as 0·125 per cent. causes the maximum improvement.[2]

Organic bonds are seldom used for silica bricks.

The proportion of bonding material, whatever kind is used, depends largely upon the siliceous material employed. The purer the silica rock used in the ground-mass, the greater must be the proportion of added bonding agent.

Substances other than bonds are sometimes added to the siliceous material in order to produce bricks with special properties. Thus, the addition of 2 to 20 per cent. of graphite is sometimes made, in order to give the bricks a dense structure combined with high conductivity of heat. Great care is essential that only suitable material is sent to the grinding plant; it is much easier to separate unsuitable matter at first than after the rock has been ground. Bildt and Ashworth, in 1891, patented the use of a mixture of 4 parts of silica to 3 parts of burned black manganese oxide to form a silicate of manganese when the furnace is in use. They claim that this mixture, whilst really acid, has the property of removing all the silicon, but no phosphorus, from steel.

Accelerators.—The inversion of quartz into cristobalite and tridymite is essentially due to maintaining it at a high temperature for a sufficient length of time (see p. 160). Various substances, known as *accelerators* or *mineralisers*, increase the rate at which silica is inverted. The most powerful of these accelerators is sodium tungstate, but its use on a commercial scale is regarded as impracticable. *Sodium silicate* is a good accelerator and also a useful bond (p. 415), and tends to reduce spalling. Its chief disadvantage is that it lessens the refractoriness of the brick, but it is possible to obtain a good accelerating effect with so small a proportion of sodium silicate that the refractoriness is not appreciably lowered. Other accelerators include:

Carbonates of lithium, potassium, and sodium.

Phosphates of sodium, potassium, and calcium (p. 160); also phosphoric acid. Sodium metaphosphate[3] aids the formation of tridymite, but calcium metaphosphate tends to form cristobalite.

Phosphorus vapour—generated by adding small quantities of phosphate rock and sand to the fuel at the back of the kiln fires—has been claimed by C. J. Crawford as rapidly effecting inversion of the silica (U.S.A. Pat. 1,477,810—1923).

Chlorides, including common salt and ammonium chloride (sal ammoniac).

Fluorine compounds—particularly sodium fluoride, sodium silicofluoride, and cryolite—are good accelerators and do not reduce the refractoriness as much as might be expected, because the fluorine tends to be volatilised as silicon tetrafluoride (see Eng. Pat. 485,871—1936).

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[1] For the evaluation of sulphite lye see Edwards and Clephane, *Trans. Cer. Soc.*, 1932, **31**, 417.

[2] Whittemore and Bull, *J. Amer. Cer. Soc.*, 1937, **20**, 261–5.

[3] Chadeyron and Rees, *Inst. Gas Eng.*, *28th Report*, 1937, p. 68.

Acids stable at high temperatures, such as phosphoric, tungstic, molybdic, and boric acids and their salts.[1]

Borax is very effective above 800° C., but tends to produce a low refractoriness-under-load.

Iron oxide.—The addition of 3–9 per cent. of ground iron or iron oxide to the silica used for making bricks was patented in 1931 (Eng. Pat. 369,312), but the use of ferric oxide as an accelerator was mentioned in a lecture by J. W. Mellor in 1919 (*Gas World*, 5th April 1919, p. 23 C.S.). Ferrous oxide is a better accelerator than ferric oxide, especially in the presence of a little lime.

Tridymite crystals have been patented as an accelerator in Eng. Pat. 387,194 (1932), but Salmang and Wentz failed to get any results from their use. Indeed, " seeding " (adding a minute quantity of the substance desired) seems useless, as it should be done just prior to cooling, when the bricks are largely inaccessible.

Silicates, such as felspar, calcium silicate, glass, olivine, etc. Soda felspar is superior to orthoclase (potash felspar) as an accelerator.

Salmang and Wentz[2] have recommended the addition of a glass or frit corresponding to $Na_2O.Fe_2O_3.3SiO_2$ in amount sufficient to raise the Na_2O content to 1·5 per cent. and the Fe_2O_3 content to 1·5 per cent.

Slags act like glasses and frits.

Prussian blue is an iron compound and probably acts like iron oxide.

Barium oxide is a good accelerator, but the product $BaSiO_3$ is objectionable as it melts at 1265° C.

Magnesia is a fairly good accelerator; it forms olivine or forsterite in the bricks.

The addition of lime, soda, potash, iron oxide, magnesia, phosphates, or a molybdate to silica rock to facilitate the formation of tridymite was patented in 1930 (Eng. Pats. 366,114 and 387,243). Eng. Pat. 455,526 (1937) specifies the addition of 2 per cent. of olivine or other magnesium silicate.

According to Nieuwenburg and Nooijer,[3] lime, magnesia, baryta, lead oxide, zinc oxide, and common salt have no accelerating effect, but Scott (p. 160) has reached a different conclusion. *Zinc oxide* makes silica bricks more resistant to slag. It forms zinc orthosilicate with silica and zinc spinel with any alumina present. It is less active as an accelerator than are iron compounds.

Flint dust and other forms of amorphous silica are good accelerators if very finely ground. They probably owe their value to their ready combination with lime, soda, and other impurities, and resulting rapid formation of a molten matrix in which quartz can dissolve and afterwards recrystallise.

Mica is also a good accelerator—probably for the same reason.[4]

Most of the *impurities* in silica bricks act as accelerators, though some are much feebler than others.

Steam is an accelerator: it lessens the viscosity of molten silica, speeds up reactions which would be very slow without it and increases the tendency to form crystals, but it is not nearly so effective as some other accelerators.

Some *bonds* (pp. 412–420) also act as accelerators.

The quantity of accelerator required is usually very small and seldom exceeds 2 per cent. It is least effective with coarse grains and at a lower temperature than 1300° C.

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[1] The use of 0·45 per cent. of these acids and salts was patented in 1920 (Eng. Pat. 159,865).

[2] *Ber. deut. ker. Ges.*, 1933, **14**, 141.

[3] *Ber. deut. ker. Ges.*, 1928, **9**, 492.

[4] Wood, Houldsworth and Cobb, *Trans. Cer. Soc.*, 1925–26, **25**, 289–308.

The objections to the addition of an accelerator are:

(1) It increases the fusibility and reduces the refractoriness of the bricks.

(2) It is difficult to ensure a uniform distribution and therefore a uniform inversion of the silica.

(3) Efflorescence on the bricks may be produced from an excess of accelerator.

The precise action of an accelerator is not fully known. It appears to be due to the formation of an easily fusible material in which the quartz gradually dissolves and afterwards recrystallises as cristobalite or tridymite. This is not the whole story, however, or soda would be the best accelerator; nor does lime work wholly as a flux and a solvent.

The *product of the inversion* depends largely on the accelerator or mineraliser present and on the temperature and duration of heating. With pure silica, cristobalite is chiefly formed, but with impure silica or in the presence of a mineraliser—particularly sodium compounds—tridymite is also produced. Ammonium chloride appears to favour the formation of cristobalite.

Selecting a Silica Rock.—For the production of silica bricks the most satisfactory rock is one having:

(i) A high refractoriness (Seger Cone 33 or above).

(ii) Less than 5 per cent. of impurities. Different impurities have different effects; thus, lime compounds aid the formation of cristobalite, whilst iron compounds assist the formation of tridymite, which is preferable. Consequently a moderate percentage of iron oxide is not objectionable.

(iii) The ability to undergo almost complete inversion to cristobalite or tridymite in a single firing (*e.g.* in 100 hours' heating after attaining a red heat). Massive quartz will seldom do this; some quartzites and flints are readily inverted, particularly in the presence of iron oxide.

(iv) No tendency to break in pieces during or after the first heating.

Rocks having some, but not all, of these properties can be used under certain conditions, but the cost of treatment will be greater than with a more suitable rock, and the difference may be so large that the sale of the bricks under competitive conditions is unprofitable.

Preparing the Rock.—If the silica rock or ganister has been carefully selected it will not require purification. Sometimes, however, it is necessary to wash it so as to remove loosely adherent impurites. This washing is readily effected in a rotary drum, along which the material travels, whilst the water and impurities travel in the opposite direction. There are obvious advantages in crushing the rock before washing it, but this is seldom attempted. Selected rock is usually better than crudely washed material, and should be used wherever possible. Where the raw material is in the form of sand, washing is sometimes essential.

Le Gall du Tetre has found that by washing silica rock with dilute hydrochloric acid and then with water a large proportion of the iron compounds present may be removed and the refractoriness of the rock correspondingly increased.

Preliminary Calcination[1] is essential if the greater part of the silica cannot be converted into cristobalite or tridymite during the time the bricks are burned whilst in process of manufacture. This is particularly the case when quartz (*e.g.* felsite, as distinct from quartzite) or very coarse quartzite is used. The temperature to be attained and the duration of heating should be determined experimentally, and ample allowance made for the greater time required

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[1] The calcination of silica before making it into bricks was patented in 1934 (Eng. Pat. 426,157).

for the heat to penetrate to the centre of the lumps used on a commercial scale. The cost of this preliminary calcination is fully as great as that of burning the bricks, and may be much greater when the raw material is a massive quartz;[1] it is very slightly less for veined quartz and much less for some readily inverted quartzites and for flint and chalcedony. For this reason few brick manufacturers can make a profit from the use of massive quartz or of felsite, particularly in a country where they would be in competition with firms using quartzites which need no preliminary calcination.

As an instance of what may be required in the case of massive quartz it may be noted that, according to R. P. Hever (Eng. Pat. 391,858), it is necessary to calcine quartz until the specific gravity is less than 2·38 and the individual particles have been "coalesced" into larger ones through vitrification (this may involve heating the raw quartz up to 1470° C.). The calcined material is ground and screened, only the following sizes of particles being used:—

(*a*) 45 parts of material coarser than 30-mesh,—

(*b*) 55 parts of material finer than 50-mesh.

The intermediate size is omitted. The bond should consist of less than 3 per cent. of sodium silicate, and the pressure employed in shaping the bricks should be 2000 lb. per sq. in. applied for 0·5–1·0 second. When dried the bricks should have an apparent density of 1·85. It is advisable to complete the inversion into cristobalite or tridymite as far as practicable; calcination for a short time or at a lower temperature than 1450° C. is seldom satisfactory, because the greater part of the inversion occurs at a high temperature and after prolonged heating.

The extent of the inversion can be roughly ascertained from a determination of the specific gravity of the powdered material; it should not exceed 2·38. A more accurate but more difficult petrographic method is described on p. 807.

The calcination may be effected in a vertical shaft-kiln, a down-draught kiln, a Newcastle kiln (fig. 61), or a continuous kiln. The last-named is the most economical in fuel, but the first has the lowest labour cost, because the rock is merely fed in at the top and withdrawn at the bottom. The heating in a shaft-kiln is never uniform and a considerable proportion of the output must, usually, be re-burned. *Fusion* in an electric furnace is also practicable.

Some manufacturers calcine only a portion of the material; this is done on the score of cheapness, but it is not a sound practice.

The proper calcination of silica rock effects the following changes:—

(i) It converts a large proportion of the silica into tridymite or cristobalite, which are the most suitable forms of silica for use in silica bricks.

(ii) It oxidises some of the impurities and changes their colour, so that the more impure portions of the rock may readily be detected and removed.

(iii) It produces a rather softer form of silica and so slightly reduces the cost of grinding.

(iv) It may reduce the mechanical strength of the finished bricks, but this is not necessarily an objection.

(v) Any clay or other "natural bond" present may be destroyed, so that a calcined rock may require more bond than a raw rock.

The subsequent grinding is greatly facilitated if the hot rock from the calcining kiln is *quenched* by immersion in water.

Preliminary Crushing.—The crushing of silica rocks is difficult and costly on account of their hardness and the wear and tear on the machines, so that it requires both skill and ingenuity to reduce such rocks to a suitable size with a

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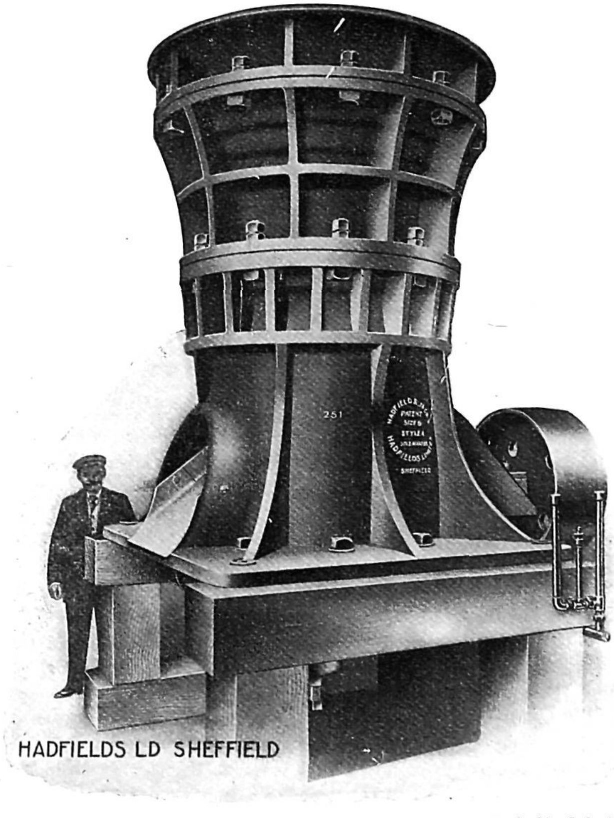
[1] The use of quartz which has been calcined until its specific gravity does not exceed 2·38 was patented in 1930 (Eng. Pat. 391,858).

minimum of expenditure. This is best accomplished by the use of either a jaw-crusher or a gyratory crusher (fig. 95). Both of these types are very popular, though perhaps the jaw-crusher has the advantage in that for equal output it is usually capable of taking larger pieces of rock than the gyratory, though in one of the cement works designed by Edison a gyratory crusher is used which will deal with pieces 4 feet by 2 feet by 2 feet! Whichever form of machine is used for the preliminary crushing, it should be of such a size that it can crush the largest pieces likely to be delivered to it. If many pieces have to be broken by hand, the value of the machine is correspondingly reduced, yet many firms make the mistake of using a crusher with much too small a hopper for their purpose. It is far cheaper to have an excessively large machine working well below its capacity, but taking all the material as it comes from the quarry, than to have a smaller one working at nearly full capacity, but having to be suppied with material of which 10 per cent. has to be broken by hand because it is too large to enter the machine. The clogging of the crusher means loss of time and low output, and should, therefore, be avoided as much as possible by the use of a sufficiently large machine.



Hadfields, Ltd., Sheffield.

Fig. 95.—Gyratory crusher.

In order to avoid an excessive amount of dust from the crusher, chutes should be employed to carry the raw material into the machine, and a water-spray or steam-jet used to damp the material slightly; an excess of water should be avoided.

In the preliminary crushing, the rock should be reduced to about the size of walnuts (*i.e.* about ¾ inch diameter), as pieces about this size may be dealt with satisfactorily in almost any kind of fine-grinding mill without serious loss of power in the latter, whereas the same mill when supplied with pieces 2 inches or more in diameter may easily require 25 to 30 per cent. more power. It is not, however, economical to reduce the whole of the rock to powder in the crushers, as the amount of power required would be excessive.

As a rule, for an output of not more than 2 tons per hour, about 15 horse-power will be required with a good crusher. It is desirable to have the crusher arranged so that it can be worked separately from any other machinery when required. As minor repairs are frequently needed, it is very desirable to keep a store of crushed material ready in case of a breakdown at the crusher, and duplicate parts should always be kept in stock unless a second crusher is available.

The crushed material should be delivered automatically to the fine-grinding mill. One of the best methods is to have the crusher placed above the fine mill, so that the crushed material is delivered on to a platform, which acts as a temporary store from which an automatic feeding device may be arranged to supply the fine mill, or the material may be shovelled into the mill as required.

Grinding.—Two methods are available for grinding the siliceous materials to a powder, consisting of sharp or angular grains of suitable sizes, namely, "dry grinding" and "wet grinding." The dry-grinding method has the advantage of enabling the material to be passed over screens of various mesh, so that the material may be properly graded, whereas the wet-grinding method does not permit this being done on a large scale.

For *dry grinding*, ball mills, tube mills, and pendulum mills are not satisfactory, as they tend to produce rounded grains instead of angular ones; but where it is desired to have some extremely finely powdered silica present, one of these mills is excellent for the production of fine powder. Ordinary ball mills, which consist of a rotating cylinder, containing the material to be ground, together with flint pebbles or steel balls, may be used, especially in conjunction with an air separator; but the most economical mill for grinding silica rocks to powder is the Hardinge conical ball mill, in which a plain cylinder is replaced by one consisting of a short cone, with its base connected to that of a long cone. This double conical cylinder is partially filled with balls of various sizes, the largest being at the point of greatest diameter. Material is supplied to the mill through the small end of the short cone, and as the mill rotates and the grinding proceeds, the fine material passes into the long cone, and is crushed by successively smaller balls, until it is sufficiently finely ground to pass out at the smaller end of the long cone. The action of the mill is continuous and progressive, the large balls acting on the coarse material and the smaller ones on the finer grains, so that no energy is wasted. The makers of this mill claim that it has the following advantages: (*a*) greater output per horse-power; 1·7 tons of silica passing entirely through a 300-mesh sieve can be produced with 28·8 horse-power, whilst, with softer material, a still greater output is possible; (*b*) a greater reduction of labour costs; (*c*) continuous operation; and (*d*) lower consumption of grinding balls.

For producing angular grains, the most suitable grinding appliances are edge-runner mills of the revolving pan type, which are used in connection with two screens to separate the ground material into three portions—

(*a*) Particles between $\frac{1}{8}$ and $\frac{1}{4}$ inch diameter.
(*b*) Particles between $\frac{1}{25}$ and $\frac{1}{8}$ inch diameter.
(*c*) Fine powder.

These three grades of material are (later) mixed in suitable proportions.

Pan mills do not create a sufficient proportion of fine dust to produce the best silica bricks, so some material must usually be ground in a separate mill—preferably a ball mill—and added, later, to the product from the pan mills. This involves a great expense in grinding, but the bricks are much superior to those produced from silica ground exclusively in a pan.

The edge-runner mill used for dry grinding should be strongly built, the runners should be as heavy as possible, and the perforations in the pan should not be more than $\frac{1}{4}$ inch diameter. Some manufacturers prefer to have these perforations only $\frac{1}{8}$ inch diameter when new, as they rapidly become larger through wear. Silica rocks, being harder than clays, require edge-runner mills of heavier construction, but in other respects of the same character as those described on p. 264 *et seq.*

It is always desirable to supply the material to the mill in pieces of suitable size; pieces which are too large choke the mill or reduce its output, and tend to cause more dust to be blown about as a result of the additional vibration caused. Each material should be tested separately in order to determine what size can be treated most effectively in the mill.

The chief disadvantage of grinding dry silica is the danger to which the operators are exposed on account of the dust which rises from the machines and causes *silicosis*, which, in some cases, is fatal. The dust difficulty may be avoided, to some extent, by enclosing the mills; but this is difficult and seldom satisfactory. Pendulum, ball, and other "enclosed" mills are not suitable, as they produce too large a proportion of rounded grains. It is, therefore, customary to employ the wet method of grinding.

The ground materials should be stored in large bins or silos of a hopper shape, so that the material can be removed from the bottom when required. When the crushed rock, consisting of grains of different sizes, is fed into the bin from a shoot, the coarser material tends to separate from the finer grades, and may thus cause trouble on account of the irregular nature of the mixture withdrawn from the store. This may be largely avoided by moving the shoot from time to time, and still better, by storing the different grades of material in separate bins.

If the material is at all moist, it may cause the screens to become stopped, and an air-separator may then be substituted. This appliance cannot be choked by a moist material, but it is useless for one which is very wet.

Wet grinding is preferably effected in edge-runner mills with a solid pan and runners of moderate weight. There are two patterns of such mills, namely: (*a*) that in which the pan is stationary and the runners follow one another around a central axis (chaser pan mills), and (*b*) that in which the runners merely revolve on their own axis, and the material is passed under them by causing the pan to revolve at a suitable speed. In both kinds of pan mill the grinding and mixing are effected simultaneously. These mills must be fed in batches, attempts to use mills of this type as continuous mixers not being satisfactory with material for making silica bricks. The usual charge is about 600 to 1200 lbs., which is treated for about 20 to 30 minutes in the mill. No pieces in the charge should be more than 1 inch diameter.

The mills may be either under- or over-driven, both patterns having their own supporters, and several modifications of each type are in use. In some of the more recent machines, each runner is carried on a separate fork, which is pivoted on to a stout shaft at the back of the mill. This arrangement has the advantage that when a piece of hard material passes under one runner, the other is not affected as in the older type of mill, with the result that it continues to have its whole tread on the pan, and is not lifted sideways and so prevented—even momentarily—from grinding properly. The use of a separate support for each runner considerably reduces the wear and tear on the mill.

The runners for silica mills should be made in two parts, and consist of a cast-iron core with a chilled metal, or preferably steel, rim, which is fixed to the core by means of wedges of hard wood. Although steel rims are costly in the first instance, they are cheaper in the end, as they are so much more durable than chilled metal. Moreover, they preserve a rough surface when in use, and thus grip the material better and increase the output, whereas the chilled metal tends to wear smooth and the rollers slip on the material to be ground. To secure the best results, the rims of the runners should be renewed as soon as about 1 inch of metal has been worn away in any one part. The centre usually wears more rapidly than the edges.

The runners should be of medium size, as those more than 6 feet in diameter and 20 inches wide are not so efficient for silica. The best dimensions for runners for milling silica are 5 feet to 5 feet 6 inches diameter, 16 to 18 inches wide, and weighing about half a ton. Such a mill with a charge of 750 to 900 lbs. of silica (all the pieces of which are less than 1 inch diameter) should work steadily with an output of 1 ton per hour, the mill being filled and emptied three times each hour, and requiring 25 to 30 horse-power, according to the nature of the material and the amount of moisture in it.

The emptying of a pan mill is usually effected by hand, assisted by some simple device. The long-handled shovels which are so largely used are effective but rather risky, and, therefore, undesirable. No wholly satisfactory method of emptying revolving pans without stopping the mill has yet been devised, but if the stationary type of pan (chaser pan mill) is employed, it may be emptied by means of a hole in the pan, which is normally kept closed by a sliding door beneath, operated by a screw.

The mill should be filled uniformly, and care should be taken not to overload it or to run it with too small a charge, so that where possible a measuring device is desirable.

The duration of the mixing must be dependent on the nature of the material. About three charges per hour is usually attained when the material supplied to the mill has previously been sufficiently reduced in a crusher. This time of milling gives a maximum strength within the commercial limits of grinding. R. M. Howe and W. R. Kerr[1] found the average transverse crushing strength of a large number of bricks of varying fineness, and burned at different temperatures, increased with the duration of the grinding, in the following proportions :

Time of grinding, in minutes, . . .	10	15	20
Transverse crushing strength, in lbs. per sq. in.	440	446	499

which indicates an increase of 13½ per cent. in the strength of the bricks, if the grinding is continued for twenty instead of for ten minutes.

Wet grinding has the advantage of avoiding the production of dust, and of saving time and labour by effecting the tempering and grinding simultaneously, but it is more wasteful of power, and does not permit the accurate grading of the material. See also " Tempering."

During the past few years there has been a tendency to use a *disc crusher* for reducing the material from 1½ in. to ⅜ in. and less, and to pass the product

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[1] *Journ. Amer. Cer. Soc.*, 1922, 5, 164.

from this to a two-deck screen; the oversize is then ground in a Hardinge or other ball-mill and separated into three grades.

For hand-moulded material, the coarsely ground material is passed into a pan-mill and is subjected to wet-grinding (p. 426).

Proportioning.—Just as in the manufacture of concrete, so with silica bricks it is necessary to have a material composed of particles of many different sizes, all intermixed in such proportions that as few "voids" or spaces as possible shall exist in the finished material. To do this, it is necessary to start with material of the coarsest grade, and add sufficient of the second grade to fill the voids between the particles. Next, sufficient material of the third size should be added to fill the voids between the second-sized particles. The same method should be used with increasingly fine material until the finest powder is used and the smallest possible quantity of unfilled voids remain. Under ordinary circumstances it is sufficient to use the three sizes of material mentioned above. Experience has shown that equal measures of each of these materials will usually give good bricks, but, for the best bricks, the proportions required to fill the voids must be ascertained by direct trial. It is also desirable to determine the voids in the tempered material (after drying it), as the tempering effects some reduction in the size of the particles. In some cases, equal volumes of the second and third sizes mentioned have proved satisfactory, the use of particles larger than ⅛ inch diameter thus being avoided. No general rule indicating the proportions can apply to all cases, however, as much depends on the shape as well as the sizes of the particles and of the interstices between them. There is also a considerable variation permissible, for Dauphin obtained equally satisfactory bricks from two mixtures, of which the first consisted of 70 per cent. of material which would not pass through a No. 9 sieve, and 30 per cent. of material which would not pass through a No. 20 sieve. The mixture, when packed well together, had a porosity of about 40 per cent. by volume. The second mixture consisted of 47 per cent. of material remaining on a No. 9 sieve, 28 per cent. on a No. 20 sieve, 3 per cent. on a No. 50 sieve, and 22 per cent. on a No. 200 sieve. This mixture had a porosity of 46·4 per cent. by volume. The difference between these materials is not necessarily so great as appears at first sight.

Robinson and Rees[1] consider that the largest pieces in silica bricks should be ¼ inch diameter, and that at least 40 per cent. of material smaller than 100-mesh sieve should be present; if the bricks are to have a porosity of less than 27 per cent., some material which has been ground fine enough to pass through a 200-mesh sieve must be included.

According to Chesters and Lee[2] the second component should consist of grains not larger than one-sixth of the diameter of those forming the first component, or the former may not fill the interstices, but drive the coarser particles apart. The densest mixture obtained by Chesters and Lee consisted of

	Per cent.
¼ in.–⅛ in. grains	50
7- to 25-mesh	20
Through 25-mesh	30

It required a considerable amount of vibration to compact it, and the components had a serious tendency to segregate, so that it was difficult to use.

In the United States the quartzite is usually ground to 0–3 mm. The bricks have a moisture-content of about 10 per cent.

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[1] Birmingham meeting of the *Eng. Ceram. Soc.*, 1922.

[2] *Trans. Cer. Soc.*, 1937, **36**, 377.

Three typical sets of grain-sizes used in different German works are:

Batch	A.	B.	C.
Less than 0·04 in.	35	33	30
0·04–0·08 in.	15	13	10
0·08–0·12 in.	30	32	35
0·12–0·18 in.	20	22	25
Added before mixing			
Calcined silica rock[1]	8	15	35
Silica dust	12	15	15
	120	130	150

The average sizes of particles in the silica bricks used in British steel works are between the following:—

	A, per cent.	B. per cent.
On 6-mesh	13	9
6- to 20-mesh	28	17
20- to 60-mesh	11	25
60- to 120-mesh	14	11
Through 120-mesh	34	38
	100	100

Both these are typical gradings, not representing extremes.

The importance of careful grading is seldom realised by British manufacturers of silica bricks, but can easily be shown by determining the crushing strength of bricks made of the same material; but using a silica rock which passed wholly through a No. 200 sieve, the crushing strength was 4200 lbs. per square inch; if the same rock were crushed so as to pass completely through a No. 80 sieve, the crushing strength was just under 1000 lbs. per square inch; whilst when the rock was carefully graded, as described above, the bricks had an average crushing strength of 3000 lbs. per square inch.

The use of a mixture containing a notable proportion of very finely ground material (known as *flour*) has several advantages. Bricks made wholly of such " flour " are exceedingly resistant to crushing, but are too sensitive to changes in temperature to be commercially useful. By limiting the proportion of flour to about 30 per cent., Philipon obtained bricks with a crushing strength of 2840 to 3350 lbs. per square inch, an average expansion during the burning of 1·6 per cent., a true specific gravity of 2·4 and an apparent specific gravity of 1·9, and a refractoriness of 1780° C. Philipon also concluded that if sufficient silica flour is present, the silica mineral comprising the larger grains is relatively unimportant, and may be either a quartz or a quartzite. G. W. Mottram[2] has patented the use of 15 to 30 per cent. of siliceous material ground in water to a very fine slip, together with some of the binder, such as lime or clay, and the addition of this slip to the graded materials, the whole being then thoroughly mixed.

The " flour " or finely ground silica not only fills up the smallest voids between the larger particles, but some of it is converted into the colloidal state and so acts as a binding material, in addition to being in a state where it can react more rapidly with the lime or other basic binding agent used.

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[1] Including broken silica bricks.

[2] Eng. Pat. 123,116 (1917).

The use of a mixture of 7·5 parts of very finely ground quartz with 5·5 parts of clay and/or 1 part of lime—the whole passing through a 250-mesh sieve—with 74 parts of coarse grains of quartz, the whole batch melting below the burning temperature of the brick, was patented in 1931 (Eng. Pat. 382,913).

Instead of grinding silica rock to flour, it is often more convenient to use water-ground flint, which can be purchased more cheaply than silica flour, and has the advantage of being rapidly inverted to tridymite.

The proportion of milk of lime or other bond to be added must also be ascertained by making a number of trial bricks and examining them to ascertain what is the best proportion of bond. As previously stated, 2 per cent. of lime or soda is usually sufficient, and in a few instances—where the rock is impure—a correspondingly less proportion may suffice.

Where clay is added as a bond, 10 per cent. will usually be sufficient. Ganister contains a natural bond, so that no additional one is necessary. The use of lime is customary, however, in some districts, as it increases the strength of the bricks.

Tempering is the process for mixing the silica, binding agent, and water together to form a plastic paste. It may occur simultaneously with the wet grinding or be a wholly independent process; the latter, being preferable, is effected as follows:—

A quantity of crushed and graded rock, water, and bond to make a charge for the mill—usually sufficient for 200 or 250 bricks—is placed in an edge-runner pan mill,[1] and tempered until a uniform paste is obtained and the mass is sufficiently plastic for use. As this operation occupies some time, it is desirable to use the pan mills alternately, so as not to waste time in a manner which is unavoidable when only one pan mill is provided. Under ordinary conditions each mill will make 15 to 20 revolutions per minute, and will require an average of 25 to 30 horse-power. The duration of each tempering varies from fifteen to thirty minutes, the longer time being needed for material to be used for bricks of special shape.

Prolonged tempering increases the proportion of fine grains, but does not greatly reduce the size of the average grains, so that its effect is not so marked as is commonly imagined. The difference may be seen in figs. 96 and 97, which are from photographs by Kenneth Seaver, and show two unburned bricks which were dried and then rubbed gently so as to reduce them to their constituent grains without breaking any of the latter. The material was then placed on paper ruled in squares, each measuring $\frac{1}{10}$ inch, and photographed. Fig. 96 shows the sizes of the particles in a material which has been tempered for fifteen minutes (the usual time for bricks), and fig. 97 one which has been tempered for thirty minutes, which is the time commonly allowed for material for blocks of special shapes.

Prolonged tempering improves the resistance of the bricks to abrasion and gives increased mechanical strength, but it tends to make them less resistant to sudden changes in temperature. By prolonging the tempering sufficiently to obtain a reasonable amount of strength, yet without producing too large a proportion of very fine grains, a paste may be made which is excellent for first-class bricks.

The grain-sizes of the ground material, the proportion of water and the duration of tempering must all be kept constant. Otherwise cracked bricks are certain to be produced. Too short a tempering and one which is too long seem to be equally objectionable, so that it is necessary to ascertain, within narrow limits, what is the correct tempering treatment.

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[1] The mills are similar to those used for wet grinding and for fireclay.

The paste is taken to the moulders' benches as required, an overhead track with facilities for tipping over each of the working benches being more convenient than the use of barrows on the floor level.

The consistency of the paste must be carefully arranged to suit the moulders or pressers; it is usually similar to that of damp sand.

Hand-moulding.—Silica bricks are usually moulded by hand in steel-faced moulds, which are open both top and bottom; some moulds have loose sides. In some respects they are similar to those used for clay bricks. The mould is placed on an iron plate, which serves as a pallet on which the brick can be carried away. The iron plates corrode rapidly and mark the bricks; this is a great disadvantage. The wear on the moulds is very severe.

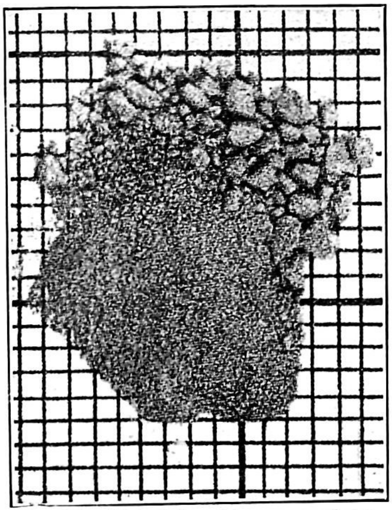

FIG. 96.—Material used for average bricks. Magnified about 1⅓ diameters.

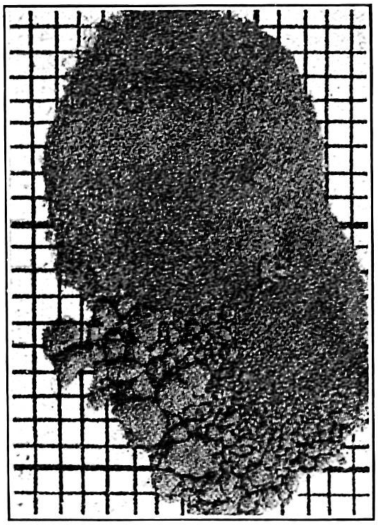

FIG. 97.—Material used in typical fine-ground shape work. Magnified about 1⅓ diameters.

A particularly good type of mould invented by William Chapman, Patent No. 17,995/12, and made by George Fowler, of Oughtibridge, near Sheffield, is shown in fig. 98. This avoids the use of an extra iron plate. Chapman's mould has end plates, which slide vertically against stationary plates, and is fitted with a pair of spring plates, so that when the mould is inverted the parts become separated slightly and the bricks are readily delivered on to the floor, no pallets being needed.

In Hurst and Jones' (1909) patent mould the sides are fixed, but the bottom is formed of a sliding plate attached to a vertical one, which forms a partition in the mould so as to make two bricks at a time. When the mould is inverted and lifted, this bottom plate and partition are drawn clear of the bricks, and when the mould is again turned to its normal position the bottom plate falls into its place. The arrangement is convenient, no part of the mould can be lost, and the value of the mould may be understood from the fact that it is largely used in several works. Some firms prefer to mould only one brick at a time, but most use double moulds in which two bricks are made at once, and in some American works a mould holding six bricks is employed; the loose bottom plate is attached to a hinged base, so that the filled mould may be inverted, the bricks delivered on to a pallet board and the bottom plate returned to its first position. The mould is then lifted off the bricks, which are held in place by a push-board. Most men find so large a mould difficult to empty properly.

Moulds for large blocks are often made of wood instead of steel or iron. Such moulds should be constructed of fully seasoned wood, free from knots and coarse-grained pieces. They may be of the usual open pattern, a board on the bench forming the bottom of the mould, or of the box pattern with a fixed bottom. The open pattern is sometimes made with loose sides held together by screws or clamps, which can be removed from the moulded block without disturbing the latter.

The moulder, provided with leather gloves to protect his hands from the action of the lime, cuts off a convenient-sized lump from the mass on his bench and throws it forcibly into the mould (which stands on an iron pallet), filling the mould.

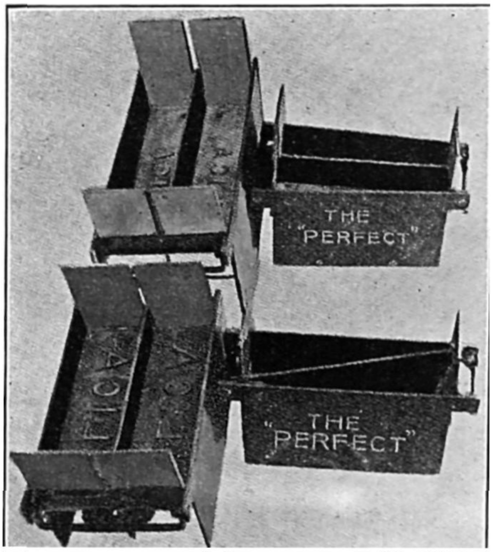

FIG. 98.—Chapman's mould.

The material in the mould is so lean that it must be consolidated by vigorous tamping or pounding with heavy wooden beaters covered with iron, and all corners and shapes of irregular outline must be rammed in by hand, just as sand moulds are made, but with much heavier blows. Unequal ramming leaves too great a variation in the density of the mass, causes the bricks to expand readily when in the kiln or in use, and tends to make them crack. Men who tamp carelessly may cause the destruction of hundreds of bricks by cracking before their fault is discovered; hence, the necessity for the strictest supervision.[1]

Any surplus material is removed with an iron straight-edge, or "strike," and a second iron pallet is laid on the mould. The moulder next turns the mould over, dresses the top of the brick, lifts off the mould, and an assistant

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[1] The use of a pneumatic rammer for tamping in a steel-lined mould is advantageous.

then carries the brick away to be dried. The material is so lean that the mould cannot be lifted like a fireclay mould; instead, the sides of the mould are loosened and fall away, leaving the brick on the iron pallet.

Before being refilled, the moulds are treated with sand, as in sand-moulding, and it is sometimes advisable to perforate the sides of the moulds with small air-holes, to prevent the brick adhering. Some moulders prefer to use crude oil instead of sand; this is more costly, but sometimes more satisfactory. Formerly, the moulds were usually " sanded " with fine silica dust swept from the floors; but some factory inspectors will not permit this, and insist on fine sawdust being substituted. In some works, the mould is laid on the floor and is filled by lifting more than sufficient paste on an ordinary shovel and throwing it into the mould from a height of about 5 feet. The material is consolidated by two or three blows from the shovel, and any surplus paste cut off with the same tool. With a little practice, a man learns to fill the moulds quite rapidly, and when the knack of doing this has been learned, the men prefer it to filling the moulds by hand.

Great care should be taken in hand-moulding silica bricks or only one good face will be produced. Better faces may sometimes be readily obtained if the bricks are dried until sufficiently hard to handle and then repressed in a suitable press. By this method, the finest particles are brought to the surface, smooth faces are produced, and the corners are sharp and true. If proper care is taken, good bricks should be obtained by the ordinary process of hand-moulding without recourse to repressing. The chief difficulties and defects are—

(i) " Squatting " due to the use of too wet a paste, or to turning the bricks out of the mould and dumping them on to the floor with too much force. If the bricks do not " turn out " readily, the mould should be sanded more thoroughly or a stiffer paste used;

(ii) Imperfect bricks due to the use of too dry a paste, which is too fusible and lacks strength, or to imperfect filling of the mould—often due to unskilled " throwing "—or to dirty pallet boards, to which the bricks adhere excessively; and

(iii) General defects caused by careless handling of the bricks in taking them from the moulds or placing them on the floor.

Large blocks of siliceous material are invariably made by hand—usually in wooden moulds—as those made in presses are liable to irregularities in texture and to be too dense to resist the sudden changes in temperature to which they are often subjected. The mould is carefully oiled with a mixture of equal measures of linseed oil and paraffin, and is then coated internally with fine sawdust. After this, the siliceous paste is thrown into the mould and is consolidated by tamping it with an iron-shod tool, the workman beginning at the sides of the mould and working gradually towards the middle. He should pay special attention to the corners, as these are usually the most difficult to fill properly. As the material becomes denser, fresh paste must be added and tamped until the mould is quite full; any excess is then removed with a knife or wire. Before adding fresh paste to that which has already been tamped into the moulds, the surface of the latter should be roughened with an iron comb or a piece of saw blade, so as to secure as intimate a contact as possible between the old and new paste. It is scarcely possible to tamp the material too much, but there is always a risk of not tamping it sufficiently. Some firms use a pneumatic hammer for the purpose, as this ensures regular blows of the requisite pressure and is less tiring to the workmen.

The after-filling of the mould, with all its drawbacks, may be avoided by placing a wooden collar about 4 inches high around the top of the mould and filling the mould almost to the top of this collar. As the tamping proceeds the material in the collar gradually disappears, so that when the tamping is finished and the collar is removed the mould is properly filled. The only objection to this method of filling is that the lower portion of the block may not be packed quite so densely as the remainder, on account of its distance away from the tamping tool. Except in blocks more than 9 inches thick, this objection does not apply when mechanical tamping is employed, and blocks 12 inches and even 14 inches thick have been satisfactorily made in this manner.

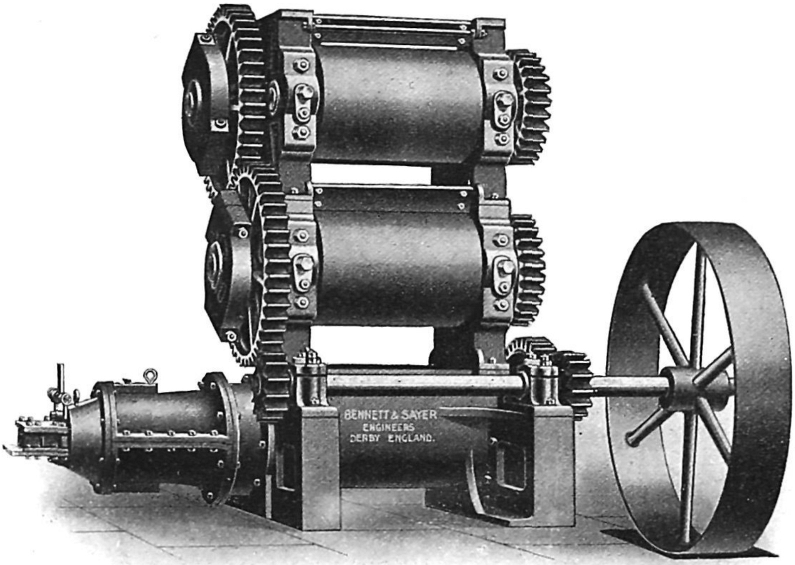
In America, much interest is being taken in a brick machine consisting of a vertical shoot about 20 feet high, above which is a bucket-conveyor and below it an endless band carrying the moulds. As each bucket discharges a definite quantity of paste, the latter falls through the shoot and fills a mould beneath in a manner similar to hand-filling. The mould and conveyor then move forward and the process is repeated. The surplus paste is automatically removed from the moulds, and the latter discharge their contents on to iron pallets. The machine produces a fair imitation of hand-made bricks at the rate of 1200 bricks per hour, though there is always a risk of the mould being imperfectly filled. The paste must be softer than for hand-made bricks. According to some users, the bricks are in every way as good as those made by hand.

Making Silica Bricks by Machinery.—There is a very strong prejudice in the minds of many makers and users against employing machinery for making silica bricks. This prejudice is, in most cases, founded on a very imperfect knowledge of the true facts, aided, in not a few instances, by an unwillingness on the part of some people to admit that machine-made bricks can be as good as those made by hand. Some men base their objections to machine-made silica bricks on reports of unsuccessful attempts with unsuitable machines or with pastes which are not of the proper consistency for machine-pressing. Others assume that because a machine-made brick is subjected to very great pressure, it must necessarily be denser, and therefore less able to withstand sudden changes in temperature, than a hand-made brick. Those who make this last-mentioned objection cannot have tested the texture of many machine-made bricks or they would know that by varying the pressure or using a properly graded material, with the right amount of water in it, the density of the bricks can be made to suit all requirements, no matter how great the pressure applied.

Many of the machines used experimentally for the production of silica bricks are quite unsuited for the purpose. Indeed, no one with more than an elementary knowledge of the subject would have tried to use them. Among these useless machines are those known in the United States as *soft mud machines*, which are used fairly extensively both in America and in this country as a substitute for hand-moulding in the manufacture of sand-faced building bricks. These machines seek to imitate the hand-moulding process as closely as possible, and consist of a pug mill or tank fitted with blades which form the paste into a solid mass, and with the aid of supplementary blades force it downwards into a series of moulds placed in the machine. These moulds are precisely the same as those used for hand-moulding, but it is customary to fasten four or six together for greater convenience in handling. All four or six moulds are filled at once.

It will be observed that the paste is simply pressed into the moulds by the machine, an action which is very different from the " bump " in hand-moulding, and it is not surprising that the moulds are filled irregularly unless the material is well adapted for the process. Certain sandy clays give good results with these machines, but they are not suited to silica bricks, as the material is too lean; it is deficient in lubricating material (fine clay forms this in clay bricks), and variations in the resistance offered by the paste in various parts of the machine make the pressure different on different bricks and in various parts of the same brick. As compared with a moulder of medium ability, these machines do fair work and do not require skilled men to attend to them, but they will not produce the best silica bricks.

Another type of machine which has been used commercially is known as a *wire-cut* or *expression machine*. It consists of a barrel-shaped pug mill or mixer, into which the paste is fed, and out of which it passes through an opening, termed a *die*, which is exactly the size of the length and width of a brick. The band of paste expressed out of this machine (fig. 99) is cut into pieces, each the size of a brick, by means of a frame carrying tightly stretched wires. The method is excellent for plastic clays, but is not good for silica paste, as the latter is not sufficiently plastic to form a good column unless a special bond is added. This bond must be used in such large proportions that it reduces the refractoriness of the bricks. Hence, the machine is good for semi-silica bricks and some fireclay bricks, but not for true silica bricks.

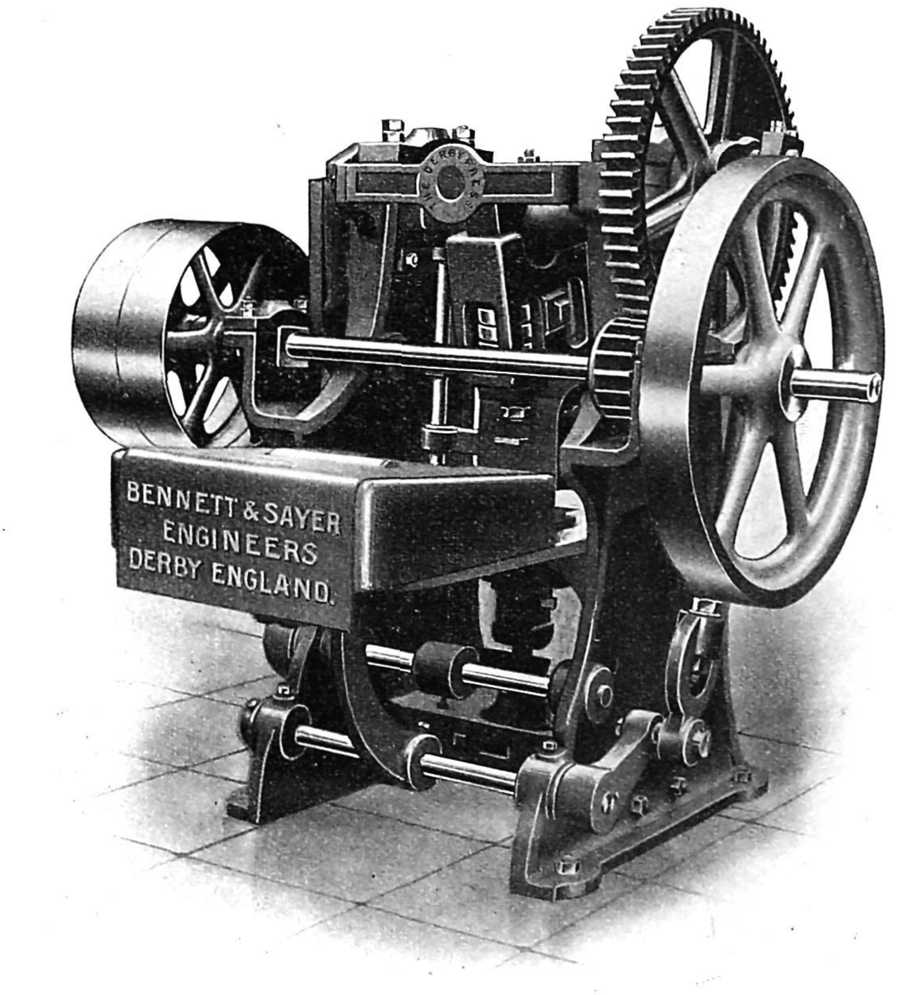


Bennett & Sayer, Ltd., Derby.

FIG. 99.—Wire-cut brick machine.

Silica bricks with a clay bond, such as those made from the siliceous pocket clays of Derbyshire, which contain 20 per cent. or more of clay, are made into clots in a wire-cut brick machine consisting of two pairs of crushing rolls and a pug mill fitted with a mouthpiece (fig. 99). The clots are then pressed in a power-driven press (fig. 100), set to give just sufficient pressure to produce a good shape without forming unduly dense bricks. Odd shapes may be pressed in ordinary hand-operated screw-presses. For very large blocks, clots may be pressed in a large power-driven press.

A further type of machine, largely used in the manufacture of building bricks, but not extensively with silica, is the *stiff-plastic press*. This consists of a preliminary clot-moulding device, which is filled by means of a pug mill, like the soft mud machines, and is then re-pressed in a steel-lined box by means of a plunger operated by a toggle lever. If the paste is made very stiff the pug mill does not fill the clot mould properly and the pressure of the press is too severe for the machine as ordinarily made. If a softer paste is used the material adheres badly to the mould and is difficult to press into good bricks. By taking great care, a man of more than ordinary ability can make good bricks with a machine of this type, but the care needed and the amount of skilled attention required are so great as to make the commercial use of



Bennett & Sayer, Ltd., Derby.

Fig. 100.—Power press for wire-cut bricks.

machinery of the stiff-plastic type quite unprofitable when unskilled men are in charge of the machine. One firm in Scotland and another in South Yorkshire make large numbers of ganister bricks in machines as shown in fig. 48.

Silica bricks may be made quite satisfactorily in a press with a rotary table. The material in the form of a lean paste falls into one of the moulds on the table, is pressed, and the brick lifted out of the mould as described on p. 282.

The *semi-dry process* is described on pp. 283 to 288.

Hand-pressing.—Instead of beating the material in the mould, the workman may use a double mould in which the bricks are formed on their narrow sides, fill it as described, remove the surplus material, then push the mould underneath the plungers of a small hand-press (fig. 101), and depress the lever, so giving the bricks an accurate shape. An assistant then removes the mould with its contents, turns out the bricks on to a pallet board, and carries them away to the drying floor.

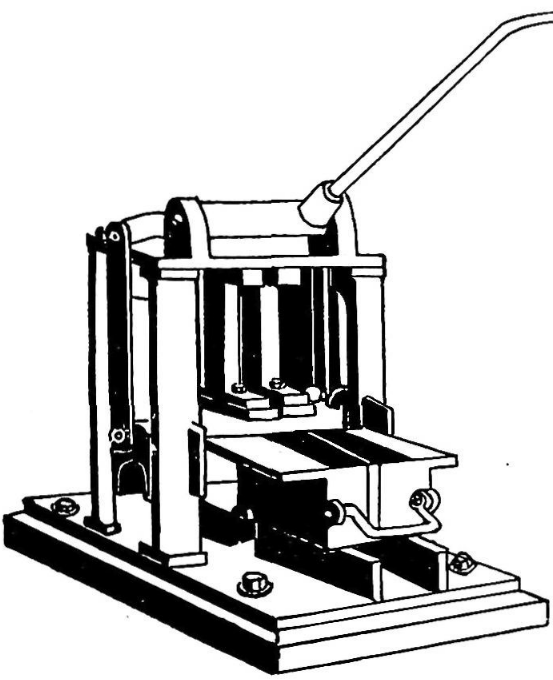


FIG. 101.—Small hand-press.

The use of the hand-press enables one man and two youths to produce 1500 bricks in eight hours, whereas, using the hand-moulding method described on p. 431, one man and one youth will only make 600 bricks per day.

The pressure exerted by the small press is so slight that the hammering the hand-moulded bricks receive is more efficient in producing sound arrises. For this reason, bricks made by means of the hand-press are considered by some users to be second-rate in quality.

The hand-presses above mentioned are so made that the pressure is applied to the face of the brick and not to its broad side. This has the advantage of needing less pressure on the lever, and it also gives the faces of the bricks a better finish. Two bricks are usually pressed at a time, though for the best results it is necessary to press only one at once.

The use of *screw presses* has not proved satisfactory for silica bricks.

Power-pressing.—Many manufacturers and users consider that silica bricks which have been made in power-driven presses are inferior to those made by hand. Recent investigations show that if the grading of the particles is properly effected, machine-pressed silica bricks are equally as good as hand-made ones and have the additional advantage of greater mechanical strength, whilst their more accurate shape gives better joints and makes the brickwork more resistant to slags, etc. According to some tests by Emery and Bradshaw, the crushing strengths of machine- and hand-made silica bricks bonded with lime were 2270 lbs. and 1630 lbs. per square inch respectively. The resistance of machine-made bricks to abrasion was also greater than that of the hand-made bricks.

The allegation that bricks which have been made in a power-driven press will spall and flake too easily to be satisfactory is only true where the grading is defective or the press is wrongly used. The fact that this method is regularly used in several of the most important works making silica firebricks is a sufficient proof of its value and practicability. The machine-pressed bricks last longer because their more accurate shape enables them to be laid better.

The only power-driven presses which can be used effectively for the manufacture of silica bricks are those in which the material is worked in an almost dry state. A perfectly dry powder cannot be used, because it has no bonding power, but the less water present the better it is for the bricks. To get good results the pressure applied to the material must be very great,[1] and for this purpose very powerful presses (either of the toggle lever or hydraulic type) must be employed. This enormous pressure needs very strongly built machines, and, unless care is taken in this respect, the machine will soon begin to rattle at the joints and get out of truth. Wear and tear rapidly increase, and the machine is soon spoiled. With a well-built machine, on the contrary, a long life may be expected, the wear being confined to the linings of the boxes and the plunger. These linings must be renewed frequently, as otherwise it is impossible to make the bricks of an accurate shape. As the bricks are very friable (the technical word is " tender ") when freshly pressed, it is well to have a loose pallet in the box of the press and to lift out the bricks on this. By this means there is no need to touch the bricks until they are quite dry and more easy to handle. The fine hair cracks which occur on the faces of bricks which have been subjected to great pressure are not usually worth notice, and, being only " skin deep," do not appreciably reduce the crushing strength of the bricks.

Power-pressed bricks, if properly made, have the following advantages compared with hand-moulded silica bricks :—

(*a*) The bricks are more accurate in shape, look better, lay more closely and easily with thinner joints, and, consequently, the corrosion of the joints by slags is much reduced.

(*b*) The bricks have a closer surface and so resist the corrosive action of the slags much better than the more open hand-moulded bricks.

The drawbacks are—

(*a*) Difficulty with most presses to secure uniform pressure throughout the brick and consequent production of laminations and " soft places." These can only be avoided by working with suitable presses and keeping the material

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[1] One of the best-known firms applies a pressure of 150 tons per brick, but Nesbitt and Bell have suggested that a pressure of only 1500 lbs. per square inch (or 27 tons per brick) is the most suitable for pressing silica bricks.

at just the best consistency. Several firms have entirely avoided these objections.

(*b*) Cost of power and plant.

(*c*) Stoppage of work if a machine breaks down, whereas a mould can be readily changed. If the press is properly designed for silica bricks it will not break down under ordinary conditions. In practice, this drawback is only found with presses which are too light or of unsuitable type.

Without in any way excluding other firms, we may say that Sutcliffe, Speakman & Co.'s "Emperor" press (fig. 53), Alexander & Co.'s "Hercules" press, and Whittaker & Co.'s "semi-dry" machine (fig. 51) are typical of good presses for silica bricks. Some of the apparently similar presses by other makers are not so suitable, as they are too weak.

By subjecting the wet bricks to a great pressure the water is forced to the outside, carrying the finer particles of silica with it and giving a nice smooth surface of fine texture. In no other way can this surface be obtained, yet it is essential for a durable brick. Thwacking is a fair substitute, but leaves too much to the individual workman to be wholly satisfactory. Moreover, the removal of the finer silica from inside the brick produces a very satisfactory brick, namely, one with a fine close face and a very porous interior. The close face resists corrosion and abrasion and the porous interior gives the bricks power to withstand sudden changes in temperature.

The use of very powerful "semi-dry" presses has greatly increased during the past few years, and pressures of 30 tons per brick are in regular use, whilst 270 tons per brick is used by some firms.[1] The "President press," made by Wm. Johnson & Sons, Ltd., Leeds, has been extensively used for other non-plastic materials, such as magnesite and chrome ore, as well as for silica bricks.

One of the difficulties associated with pressing semi-dry materials is the inclusion of air between the particles. This air tends to form "lines of weakness" in the bricks. Much may be done by applying several pressures in succession and releasing the air between each. Alternatively, most of the air between the particles may be removed by using perforated plates in the press-box and connecting these to a vacuum pump.

Power-pressed silica bricks owe part of their greater durability when in use to their accurate shape, which enables them to fit more accurately into the brickwork and avoids the taking up of stresses by small portions of the bricks. The interlocking of the angular particles caused by the intense pressure is, however, the chief cause of their strength.

In several large works in the United States the "Anaconda" method is used. In this, the paste is made as wet as a slop-moulding clay paste. It is then slop-moulded direct on to pallets, each of which holds six bricks. These clots are dried until they are hard to dent with the finger and are then put through a heavy re-press and again placed upon pallets. In a modification of this process in use in this country, the bricks are moulded one at a time in an ordinary hand-mould, and after allowing to stiffen on a cold floor they are re-pressed in a power press. By this method, it is stated, 200 to 300 more bricks can be made per day than by the use of a hand-press only, and the bricks are stronger. About 1440 bricks are made per hour.

Contrary to what might be expected, the breaking, in the re-press, of the bond produced by the preliminary setting of the lime does not appear to affect the final bond of the goods.

When the bricks are thoroughly dry, they are extremely hard, so hard,

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[1] R. B. Sosman has stated that the pressure should not exceed 8 tons per sq. in., which is equivalent to 324 tons per brick.

in fact, that it is possible to drop them on their ends from a height of three feet without breaking them. Their hardness makes the breakage between the dryer and kiln very slight.

This method of working produces a brick which is so much denser than the ordinary hand-made silica brick that it weighs two to four ounces more than the latter. The number of damaged bricks is also less, and the bricks are tougher and less brittle.

G. Weintraub and H. Rush (Brit. Pat. 20,348, 1912) consolidate the silica by heating it electrically whilst it is under pressure. This process appears to be worth further attention.

Drying.—The danger of silica bricks cracking during the drying is much less than with fireclay bricks, so that they may be heated rapidly from the first. It is, in fact, better to heat them rapidly during the drying, as this brings about a more complete hardening than would otherwise be the case, and the bricks are easier to place in the kiln. The time occupied in drying varies with the type of dryer employed. In most cases, 18 to 24 hours should be sufficient, and sometimes the drying is completed in 12 hours.

Too short a time is undesirable, and sometimes many bricks are broken by lack of care in this direction. Care should be taken not to let the outside of the bricks harden too much whilst the interior is still wet. To prevent this, the humidity of the air in the dryers must be carefully and skilfully regulated. Large blocks should be dried much more slowly and with most careful control of the humidity of the air in the dryers.

Usually, the bricks are dried on floors heated by fires or steam, but, though popular, this arrangement is not economical. It is much better to employ a series of portable iron shelves or pallet boards, arranged in sets of ten, one above another. Gangways are left between each set of shelves to provide facilities for filling them and for taking the bricks to the kiln. The first cost is heavy, but is soon repaid by the great number of bricks which are dried without appreciable cost.

In some parts of the country, and especially in South Wales, the newly made bricks are placed in stoves of large dimensions, where they are baked for one night by fires which are lighted after brickmaking has ceased for the day. These stoves are usually hotter and dustier than the worst hot floors or "flats," and should be avoided as far as possible. It was thought, at one time, that, with the introduction of tunnel dryers, stoves and drying flats would soon be a relic of the past, as there is less handling and carrying of the bricks, and all the discomfort and dust of hot stoves and steamy drying floor are avoided. Unfortunately, tunnel dryers with cars have not been very satisfactory for silica bricks, as the bond in the wet bricks is very weak and many defects are caused by slight jars. Hence, long tunnel dryers are scarcely likely to be satisfactory, as some vibration is certain to occur in any tunnel dryer, though it might be rendered harmless by the use of sensitive springs like those on off-bearing barrows. This difficulty may be avoided by the use of long tunnels without cars, but the moulders find that these are uncomfortable, and so they do not produce so many bricks as when working under better conditions. On the other hand, power-pressed bricks are not so sensitive to vibration, and can be dried in a tunnel dryer heated by steam in 12–15 hours with no serious risk.

J. Holland and W. J. Gardner have suggested the use of a tunnel dryer in which the bricks are placed on trays running on steel rollers.

It is important that bricks and blocks of silica should be handled as little as possible during drying, as they are very friable and easily damaged. As soon as they are dry they should be taken to the kiln, as they soon spoil when exposed to moist air.

Dust Prevention.—Owing to the Government regulations regarding the manufacture of silica bricks, greater care must be taken to avoid the production of dust, as this is injurious to the health of the workers. Newly made bricks are harmless, but as they dry they become more and more friable, and when removed from the dryer some dust is rubbed off and settles on the floor. Each time the floor or dryer is emptied and before a fresh lot is placed in the dryer, the dust should be removed by first damping the floor and then sweeping it. Ordinary dry-sweeping must not be employed, as it causes the dust to rise, and so may cause silicosis amongst the workers. The damping, however, must be carefully managed, or it will cause a cloud of fine dust to rise; the sweeping must follow within a few minutes of the damping and before the floors are dry. All sweeping should be done with some tool kept constantly wet by dipping in water. A rubber squeegee, a scraper, or a shovel may be used to greater advantage than a wet brush, but the worst of all these devices is that they leave an irregular surface on the floor which tends to spoil the bricks. Dry-sweeping or a vacuum cleaner avoids this, and is quite safe if the worker concerned wears a suitable respirator. Corresponding precautions should also be taken in filling and emptying the kilns.

Taking to Kiln.—The bricks should be taken to the kiln on barrows provided with good springs. Some makers use large barrows and a single layer of bricks; others prefer smaller barrows, on which the bricks are stacked in layers with a strip of felt between each. The barrows should run on iron strips, as this facilitates a speedy transport and prevents the floor and the bricks from being damaged.

Setting.—The bricks are set checkerwise in a similar manner to fireclay bricks, those of lower quality being placed near the bottom. Due allowance must, however, be made for the fact that silica bricks expand when heated, and they must not be set quite so tightly nor so high as fireclay bricks. The burned bricks when correctly placed will be $\frac{5}{8}$ inch apart. To prevent the feet of the men damaging the bricks, a few sacks should be laid on the lower courses and a board or plank placed on the sacks. The men should stand on the board and not on the bare bricks.

It is usually wise to set a few fireclay bricks near the top of the bags, as the silica bricks are sensitive to sudden contact with flame, and the fireclay bricks, being less sensitive, can be burned with less risk of damage. Large silica blocks and those of unusual or irregular shape should not be placed near the fire-boxes nor where they are required to withstand much weight, nor in parts of the kiln where they are subjected to sudden changes in temperature.

At intervals of 3 feet or so in the height of the kiln, horizontal flues should be left, corresponding to spy-holes in the walls of the kiln. Through these, the burner can see how the heating progresses; they also form convenient places for Seger cones (fig. 83).

Owing to the Government regulations for the safeguarding of the health of the setters, precautions must be taken to avoid unnecessary dust. The ordinary method of filling a kiln is for one man, standing by a barrow-load of dried bricks, to take two bricks and throw to the man who is stacking. A trail of fine dust follows the bricks in their flight and, consequently, is unhealthy, so that the practice of throwing bricks from hand to hand should be prohibited. A better method of setting consists in the man at the barrow handing the bricks separately into the hand of the setter, so that there is no trail of dust. The men, who are employed on piecework, do not earn any less through adopting this simple precaution. At one factory, a bucket of water is also kept at each kiln, from which the kiln floor and also the bricks if they come too dry from the flats are sprinkled; but whilst there is not much objection to sprinkling the floor of the kiln, the bricks themselves should not be wetted.

When the kiln is full, the door is built up and burning may be commenced.

Kilns.—The kilns used for silica bricks are usually single ones with a capacity of 80 to 100 tons. These kilns are of the round down-draught type, but if the output is sufficiently large it is far more economical to use continuous chamber kilns. In other words, kilns which are suitable for fireclay bricks are equally satisfactory for silica bricks, though they require modification in some instances.

A very popular, but by no means ideal *single* kiln for silica bricks, is a round one, 20 feet inside diameter, 10 feet to spring of crown or dome, and 16 feet total height. Around the outer walls are eight or ten fires and inside are the same number of bags, which may be as low as 4 feet high, or may reach to the spring of the crown. In the middle of the floor is a well 2 feet 6 inches square, leading to the main flue, of the same size. From the well a series of horizontal flues, each 9 inches wide, is built right across the kiln, and on these the bricks to be burned are set. If the heating power is found to vary in different parts of the kiln, this is modified by making these flues narrower or wider at those parts, according as less or more heat is required. These flues are cleaned out occasionally by means of a small shovel.

In another form of round down-draught kiln which has proved very satisfactory for silica bricks there are eight radial flues below the floor, each of these flues terminating in a vertical one built in the walls of the kiln. These flues all discharge their contents into a conical chimney built on the top of the kiln, which thus resembles a pottery oven or cupola in shape.

The kiln is coal-fired, but the use of producer gas or semi-gas firing is advantageous.

Single down-draught kilns give very uniform heating, but are wasteful in fuel; to avoid this, the kilns should be connected and worked in series, or a continuous kiln should be employed where the output is sufficiently large.

A *continuous* kiln for silica bricks must be specially designed for the purpose. It must consist of a series of separate chambers, each capable of being worked independently. The whole of the air required for the combustion of the fuel must not pass through the cooling chambers; part may pass through flues in the arch, floor, or walls, thereby cooling the latter without coming into contact with the cooling bricks. The heat from the goods will pass by radiation and convection into the hot-air flues, so that the cooling will be effected satisfactorily and an ample supply of hot air will be provided.

The chief objection to continuous kilns for silica bricks is the slow rate at which such bricks require to be cooled. Unless the continuous kiln is very long it is difficult to work it satisfactorily and yet cool the bricks at a sufficiently slow rate. By the use of suitable flues to supply air to the fuel direct from the atmosphere, this difficulty may be overcome.

Suitable continuous kilns are described on pp. 296 and 300 to 312.

When burning silica bricks in a 20-chamber continuous kiln, the chambers should be occupied as follows:—

No. 1 being filled.
Nos. 2 to 6 being "smoked."
Nos. 7 and 8 being pre-heated.
No. 9 under full fire.

Nos. 10 and 11 being fired to continue the inversion of the silica and to prevent cooling too quickly.

Nos. 12 to 18 cooling.

No. 19 being emptied and No. 20 empty.

A *tunnel kiln*, provided it is sufficiently long and is well designed, has many advantages over others for burning fireclay, silica, and magnesia bricks. A tunnel kiln which is too short is not economical, as it must be worked so slowly. One firm on the Continent is successfully firing silica bricks in a tunnel kiln 266 feet in length, with cars 6 feet long each carrying the equivalent of 750 English bricks, which are fired to Cone 15, one car being delivered every 2½ hours. The fuel consumption is 30 per cent. of the weight of the fired bricks.

In the United States a tunnel-kiln, 510 feet in length and holding 63 cars, burns four car-loads or 20,000 bricks each 24 hours at Seger Cone 17–18 (1480°–1500° C.) with a fuel-consumption of 20–25 cwt. of coke per thousand bricks. Most of the silica bricks in the United States are burned in large, round, down-draught kilns, each holding 100,000–140,000 bricks; the round of the kiln is 21–24 days, the actual burning period being about 10 days.

Burning.—The burning of silica bricks serves two purposes: (i) to render the volume of the bricks as constant as possible by the conversion of much of the quartz into tridymite or cristobalite; and (ii) to form a strong body of great resistance to crushing and to heat, the strength being produced by forming a fusible compound of the bond with the finer grains; this fused material then flows between the larger particles and binds them together.

The earlier stages of burning silica bricks usually present far less difficulty than is the case with clay bricks, but the high finishing temperature (Cones 15 to 18) and the very careful cooling demand that the burners must be reliable men of sound judgment and considerable skill, otherwise, the sudden stresses produced will cause the destruction of the bricks. A slow heating for twenty-four hours is followed by a quick but steady rise of temperature requiring one to two days, the firing being held for some hours when the requisite Seger cone or other "trial" shows that the finishing-point has been reached. Hence, silica bricks are fired in a similar manner to fireclay bricks, but more rapidly at first. During the burning, care must be taken not to admit cold air into contact with the bricks, as this will crack them. For this reason, only one fire-hole should be cleaned at a time.

The finishing temperature should usually be 1435° C. to 1500° C. (Cones 15 to 18), and the kiln is maintained near this temperature for eight or ten hours. Better bricks will be produced if the final temperature is Cone 26 (1650° C.), and the kiln is maintained at this for twenty-four hours, the fire-boxes being then sealed. In some American works, a temperature of 1500° C. to 1550° C. is maintained for forty-eight hours so as to ensure the production of a large proportion of tridymite, but in this country the total time of firing in single kilns seldom exceeds forty-five hours, and in continuous kilns twenty-four to thirty hours is generally allowed for the actual firing, *i.e.* excluding the time for preheating by waste gases from other chambers. The cost of reaching these high temperatures is so great that many manufacturers are content with a finishing temperature corresponding to Cones 9 to 12, but this is far too low for bricks of good quality. J. H. Dennis (Brit. Pat. 14,278, 1906) specifies the finishing temperature as that at which ganister "vitrifies without melting all the iron present."

There is a tendency in some works to attain a sufficiently high temperature in the kiln, but to stop heating too soon, with the consequent formation of an under-burned and weak core in the bricks. This can only be prevented by maintaining the kiln at a suitable temperature[1] for a time sufficiently long for the heat to penetrate to the centre of the bricks. Excessively prolonged heating should be avoided, as this tends to cause the bricks to collapse. Standard time-temperature graphs of the burning are invaluable.

The best test for the end of the burning is to remove samples from the kiln from time to time and to determine their true specific gravity. If the specific gravity could be reduced to 2·28 the inversion of quartz to tridymite would be complete; but this is seldom possible, and, consequently, when the specific gravity is reduced to 2·4 the kiln may be closed down. An alternative and more generally used method is to measure the expansion of the bricks by means of a " settling gauge " as described on p. 332. This is excellent when used in conjunction with cones or thermoscopes.

Another method of determining whether a silica brick has been sufficiently burned is to measure its length very accurately and then heat the brick gradually to a temperature of about 1450° C. to 1500° C., maintaining it at this temperature for several hours; it is then slowly cooled. If the brick has previously been satisfactorily burned, the porosity and size of the doubly burned brick should be practically the same as before. On the other hand, an underburned brick increases both in porosity and size.

Silica bricks usually require 16 to 18 cwt. of coal per thousand bricks, but by connecting several kilns or by using a continuous kiln, about half the fuel may be saved.

When the finishing temperature has been reached in every part of the kiln, the fire-holes are closed and sealed with clay paste, the damper at the chimney or leading to the next chamber is almost closed, and any other precautions necessary are taken to prevent air entering the kiln whilst it cools.

The changes which occur are chiefly—

(*a*) Removal of any moisture or organic matter.

(*b*) Conversion of lime and other bases into silicates and subsequent fusion, forming a bond corresponding to the vitrified matter in clay bricks.

(*c*) Conversion of the quartz into cristobalite or tridymite, with consequent increase in volume. The amount of inversion in British and American bricks examined by Hugill and Rees and by Norton respectively is:

	Quartz.	Tridymite.	Cristobalite.
British bricks . . .	5–25	10–45	50–75 per cent.
American ,, . . .	0–25	4–40	50–70 ,,

In many silica bricks the inversion is much less than is shown by the above figures.

The conversion of quartz to tridymite can take place only under certain conditions which are, for the most part, lacking in the manufacture of silica bricks, so that during the burning most of the altered quartz forms cristobalite, although tridymite is the stable form at the kiln-temperature. The conversion from cristobalite to tridymite takes place very slowly whilst the bricks are in use, particularly in those parts which are at a temperature of 870° to 1470° C.

Cooling.—Usually 5 to 14 days are required for the cooling to be effected satisfactorily. They may be cooled fairly rapidly to about 500° C.; it is in cooling below this temperature that they are most liable to crack or spall. If the cooling occurs too rapidly, it is possible to hear a series of sharp cracks,

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[1] It is difficult to take temperatures in the interior portions of the kiln except by cones, but these are often decidedly erratic in registering the temperatures of silica kilns, cones of higher number going down, while neighbouring ones of a lower number in the series are but slightly bent or unaffected.

like the reports of miniature pistols. Attempts to hasten the cooling are invariably risky and frequently prove to be failures. Silica bricks which have been cooled sufficiently slowly through the various transition stages are much less liable to spall than those which have been cooled less skilfully. The best that can be done is to make a small opening in the top of the kiln at a time when it is judged that no part of the contents is at a red heat. Shortly afterwards, two or more openings may be made, and the number increased daily until the kiln is sufficiently cool to be opened.

It is almost impossible to make use of the heat in the fired silica bricks, as they are so sensitive to changes in temperature that a current of air drawn through in order to cool them will cause many cracks. By using a sufficiently large number of chambers (not less than 20) to ensure very slow cooling, however, a continuous kiln can be used with complete satisfaction and great economy in fuel.

What is really needed is an arrangement for supplying air of any desired temperature to the finished goods, so as to cool them gradually, and this is best accomplished by the use of some arrangement in which hot air is used to cool the goods. This is a matter which has not received the attention it deserves, and silica brick manufacturers would do well to consider more carefully than most of them have hitherto done the claims of certain modern multiple chamber kilns and tunnel kilns, such as those described in Chapter II.

Drawing from Kiln.—As the bricks are removed from the kiln, any damaged or defective ones should be placed on one side. The remainder are sorted according to quality and hardness of burning and are then taken to the store. Silica bricks should all be the same size (unless otherwise specified). To ensure this, some manufacturers grind the finished bricks so that they do not vary more than 0·01 inch from the dimensions specified by the purchaser.

The sorting of silica bricks is equally as important as any other part of the manufacture, for unsorted bricks cannot give as much satisfaction to the user as those which have been properly arranged in groups. Many manufacturers neglect this to their own loss.

The bricks near the doorway are generally under-burned, and should be set aside and re-burned.

Less dust is generated in kiln-drawing than in the setting of a kiln, and much of it does not consist of such fine particles. Still, as the atmosphere, when a kiln is being drawn, is usually warm, promoting perspiration and deep breathing, this dust is not negligible, and the practice of throwing the bricks should be prohibited; those employed should be provided with, and should wear, suitable respirators.

Steam-heated Bricks.—Efforts to avoid the use of kilns must necessarily fail, as the subsequent heating of the bricks when in use would cause them to expand more than the builders could allow. For this reason, unburned lime-sand bricks cannot replace silica bricks which have been burned at a high temperature. (See also p. 461.)

Storage.—Silica bricks are soon damaged by water, and must, therefore, be stored under cover in a dry place. On no account must the floor on which they are stored be made of ashes or clinker. The bricks should not be exposed to frost, particularly if they are damp.

The properties of silica bricks—including Dinas and ganister bricks—differ in several respects from those of firebricks made from clay.

The *colour* of silica bricks is often an extremely pale buff, but more frequently these bricks are practically white with a slight sheen of vitrified matter, which is not easily discernible. The broken bricks have a yellow tinge, with various spots of a dark brown colour, together with a large amount of white matter and numerous holes and pores, unless the material has been prepared with unusual care.

Brown stains (*flowers*), irregularly distributed on silica bricks, are due to soluble iron compounds and can be prevented by adding a small quantity of ammonia to the tempering water.

The *crystalline structure* of a silica brick determines its quality. The best bricks are coarse-grained, contain at least 1 per cent. of titanium oxide and have a structure composed of tridymite twin crystals. The extent to which this inversion occurs depends on the nature and proportion of any impurities which act as accelerators (p. 420) and on the temperature and duration of the burning. An examination of the X-ray spectra of silica bricks by Jay and Chesters[1] showed that the average size of the cristobalite and tridymite crystals was 0·01 cm., as compared with 0·001 cm. for the raw silica (quartz).

If the original silica is very pure, the final product will be a mixture of quartz and cristobalite. If impurities are present some tridymite will probably be formed. By adding iron oxide as much as 75 per cent. of tridymite may be formed.

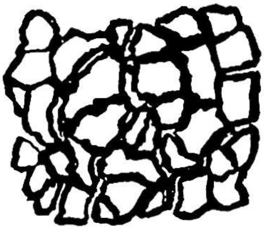

FIG. 102.—Diagram of micro-structure of ideal silica bricks.

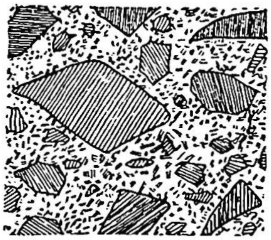

FIG. 103.—Micro-structure of Dinas brick.

The *texture* of silica bricks is readily seen with a magnifying glass to be that of a mass of small grains of silica of irregular shape cemented together with a film of glassy matter (fig. 102). Where the grains of silica are less regular in size and an excess of very fine grains is present, the structure of the brick—as seen under the microscope—more closely resembles that of fig. 103, which represents a portion of a brick made of Dinas sand used without previously crushing or properly grading[2] the raw material.

The granular mass is composed of a variety of substances, being coloured yellow by the iron present, and usually showing traces of slag, etc., and occasionally of magnetite. Its chief constituent is, however, a mass of mixed colourless tabular crystals which, in polarised light, may readily be recognised as consisting of unaltered *quartz* together with some *tridymite* and *cristobalite*.[3] Bricks made of true ganister consist of a felted mass of minute crystals of tridymite together with grains of unaltered quartz embedded in quartz glass. On prolonged burning, some of the crystals of tridymite enlarge at the expense

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[1] *Trans. Cer. Soc.*, 1938, **37**, 209–230.

[2] The proper grading of the crushed rock is essential for the best bricks.

[3] Whether tridymite or cristobalite or both are formed depends to some extent on the presence or absence of a flux and on the effectiveness of the heating. It is curious that intense heating appears to reduce complex molecules of silica to simpler ones, whilst it has the opposite effect on alumina, causing the latter to polymerise.

of the smaller ones. The conversion into tridymite is seldom complete. The various forms of silica may be recognised by the method described on p. 157.

The larger the proportion of tridymite or cristobalite in the bricks after firing, the greater will be their value and durability. The formation of these allotropic forms of silica is fully described on p. 159. The presence of tridymite is preferable to cristobalite for various reasons, and, as far as possible, a tridymite network in the bricks should be produced.

Strictly speaking, silica bricks cannot be regarded as fully burned until all the free silica has been converted into tridymite (or cristobalite), this being in the true state of equilibrium at high temperatures. In practice, this is never obtained, and the burning of silica bricks is regarded as " finished " when they have been heated sufficiently to bend a specified Seger cone or thermoscope, or have been heated for a definite time under ill-defined conditions, or have expanded to an extent which is regarded as sufficient. R. S. M'Dowell states that sixteen or seventeen burnings would be necessary to convert the whole of the quartz in an ordinary silica brick into tridymite or cristobalite, but very finely textured quartzites are much more readily converted than the coarser grained ones. In order to obtain a maximum amount of tridymite in silica bricks without unduly increasing the cost of production, they should be held at a sufficiently high temperature for a period of 40 hours, the most suitable temperature for the rapid formation of tridymite being between Cones 14 and 18 (1410° C. to 1500° C.).

English bricks seldom have more than 35 per cent. of the quartz altered, whereas in some American bricks as much as 80 per cent. is inverted, as the result of maintaining the kiln at a temperature of 1500° C. to 1550° C. for 24 to 48 hours, after what would ordinarily be regarded as the finishing-point of the firing. This prolonged soaking is very costly, both in fuel and labour, but the increased value of the bricks makes it well worth while.

It is important that the conversion of quartz should not take place too rapidly, or the cohesion between the grains will be seriously disturbed and so cause the rupture of the bricks when subjected to a sudden rise of temperature.

To be of first quality, a silica brick should have practically no after-expansion, so that it is necessary for it to be fully expanded during the first burning. This is only possible if the grains of silica are sufficiently fine so that as large a proportion of silica as possible is inverted to tridymite with one firing, in order to render them free from after-expansion. If the maximum expansion is attained, though the recognition of the actual crystals of tridymite may not be possible, the subsequent formation of the crystals may take place without risk whilst the bricks are in use. To secure these desirable properties, K. Endell has recommended [1] that silica bricks should not contain more than 15 per cent. of unchanged quartz and silicates, and that at least 5 per cent. of tridymite should be present.

The glassy matter, in the case of silica bricks made with a lime bond, is chiefly composed of one or more calcium silicates or calcium alumino-silicates, but there is no reliable experimental evidence as to the precise composition of these compounds; wollastonite and anorthite are probable constituents. After continued use, the ground-mass becomes devitrified and contracts slightly, whilst the larger grains become isotropic. Theoretically this should lead to an expansion of 20 per cent., but if the brick has been properly fired previously, most of this expansion will have occurred during the manufacture of the bricks.

The *hardness* of the bricks as a whole is not great, as they can be rubbed

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[1] *Journ. Amer. Cer. Soc.*, 1922, **5**, 209.

away without difficulty on account of the weakness of the bond. The individual grains have a hardness equal to that of quartz.

The chief cause of the bricks being too soft is due to an insufficient quantity of lime to flux the material during burning or to insufficient heating in the kiln. The silica contains no adhesive matter, and, unless sufficient fused matrix to form a bond is produced during burning, the grains will not hold together. The remedy lies in adding the proper proportion of bond, in drying the goods thoroughly before sending them to the kilns, in setting them properly, and in burning them sufficiently. Well-burned silica bricks should be sufficiently hard to " ring " well when struck. Silica bricks made with silica which has been pre-heated before being made into bricks do not give so good a " ring," when burned, as do those which are made from uncalcined silica. It is not, however, desirable to use this as a test of the quality of a silica brick, as the " ring " depends on a number of factors, some of which may affect the sound of the brick when struck, but not necessarily be harmful to the brick.

The *resistance to abrasion* is moderate: it differs with the manner in which the bricks are made. Emery and Bradshaw found that machine-made silica bricks resist abrasion better than hand-made ones. Mellor and Emery found that flue-dust penetrates silica bricks rather less readily than fireclay bricks.

The *resistance to corrosion* and to *chemical action* is sufficiently great to enable silica bricks to be used extensively in metallurgical furnaces in contact with *slags*.

The chemical reactions which occur between slags and silica bricks are clearly shown by the following: if six molecules of silica (360 parts) and one molecule of lime (56 parts) are heated together, the product at 1436° C. contains only 37 per cent. of molten material (liquid), and at 1698° C. only 50 per cent. of liquid, but if one molecule of alumina (102 parts) is added the mixture becomes completely liquid at 1345° C.

Another example is that a mixture of equal parts of slag and silica brick which melts at 1600° C. will melt at 1320° C. if only 10 per cent. of alumina is added to the mixture.

The resistance to slag depends on similar factors to those described on p. 349.

Ample resistance to slag is very important in the case of some silica bricks, especially in some metallurgical industries. To ensure this the bricks must have a moderately coarse texture and have been well burned. When a silica brick which has been seriously attacked by sand is examined, it will be found that the " hot " end (the one attacked by the slag) is usually penetrated with slag for a short distance below the surface. In this zone of attacked material and also next to it is a grey zone of cristobalite crystals and magnetite with, sometimes, a few tridymite crystals; the second zone consists of tridymite, magnetite, and a small proportion of cristobalite; the cooler part of the brick consists of cristobalite, tridymite, and quartz, the last increasing towards the unaltered part of the brick. In the hearth, fayalite and tridymite occur embedded in a dark glass, with some ferrous oxide in the hotter portions. Iron silicates are only formed when conditions are reducing.[1]

A very mobile and basic slag will penetrate and may rapidly destroy the surface of a silica brick to a considerable depth, and if the weight of adherent slag is sufficient part of the brick may break away. With bricks having very small pores the penetration is less and the effect less disastrous, unless the brick particles are so minute that they are rapidly dissolved in the molten slag.

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[1] A. Scott, *Trans. Cer. Soc.*, 1926, **25**, 339–351; von Keill and Damman, *Stahl u. Eisen*, 1925, **45**, 890.

Unaltered quartz is more readily attacked by slags than is cristobalite or tridymite, so that adequate inversion is essential in the best silica bricks.

Under oxidising conditions silica bricks are fairly resistant to iron oxide, but under reducing conditions they are rapidly attacked and form fayalite (ferrous silicate).

A low rate of destruction by slag seems to depend chiefly on (i) the formation of a viscous product which does not move about very much, and (ii) a close texture with the grains strongly united to each other. The latter may be formed when the brick is in use by the action of the slag and heat of the furnace producing a dense impermeable layer of modified brick. For the same reason a porous brick need not necessarily have a poor resistance to slag.

Under some conditions of use, silica bricks can absorb considerable quantities of slag or of alkalies and alkali salts without the skeleton or core of the brick being affected or its stability reduced. Mellor and Green [1] attribute this to the formation of an impervious protective coating on silica brick, whereas the alkali alumino-silicate compounds produced with clay are less fusible and so remain porous and easily penetrated by further alkali or slag.

The *fissility* of silica bricks is not very different from that of fireclay bricks; though the former are more brittle and more difficult for bricklayers to cut.

The *specific gravity* of silica bricks varies from 2·3 to 2·6, according as the grains of which they are chiefly composed are those of tridymite or other form of silica. The specific gravity test is of great value in determining whether the bricks have been sufficiently burned. Insufficiently burned bricks usually have a higher specific gravity than properly burned ones, owing to the fact that in the transformation from quartz to tridymite or cristobalite the specific gravity is reduced in proportion to the amount of tridymite and cristobalite produced. The best results would be obtained if practically the whole of the silica were changed into tridymite or cristobalite, in which case the specific gravity would be about 2·3. Bricks made from flint usually have a very low specific gravity, as the transformation of flint occurs much more rapidly. Flint, before burning, has a specific gravity of about 2·60 to 2·62, but on burning it is reduced to 2·22. Bricks having a specific gravity of 2·40 or less may be regarded as satisfactory, whilst those having a greater specific gravity have not been fired sufficiently long or have been burned at too low a temperature. Flint-quartzite bricks should have a specific gravity of 2·22 to 2·25.

The ordinary specific gravity bottle is not suitable for very accurate determinations of the specific gravity of siliceous materials, as it cannot be evacuated at high temperatures. A much more suitable device is a small flask with a long neck and stop-tap, such as that described by Washburn and Navias.[2]

The *apparent density* of silica bricks is somewhat less than that of fireclay bricks, but varies between limits too wide for any detailed statement to be made concerning it. This is due to the fact that so many factors—such as relative sizes of grains, closeness of packing, etc.—affect the apparent density. Curiously enough, the much greater pressure applied in machine-made silica bricks does not greatly affect the apparent density of the material. Nesbitt and Bell made tests applying pressures varying from 187 to 2500 lbs. per square inch, and found that the apparent density only ranged from 1·50 to 1·68.

The *porosity* of silica bricks varies within very wide limits, according to the grading of the material and the mode of manufacture. In practice, the usual limits of porosity are between 22·5 and 32 per cent., though in the

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[1] *Chem. Ind.*, 1938, **57**, 633.

[2] *Journ. Amer. Cer. Soc.*, 1922, **5**, 565.

author's experience a porosity of 18 per cent. ensures the greatest durability. The difference in the porosity of correctly burned bricks and under-burned ones may be as much as 8 per cent., so that badly under-burned bricks can readily be identified by this means.

In testing porosity, the bricks should be broken and carefully inspected, so that capillary pores, which are relatively harmless, may be distinguished from coarse openings, which allow destructive agents to enter the bricks.

The *chemical composition* of silica bricks, as shown by analysis, is practically that of the siliceous rock from which they are made, together with that of the bond (if any) which has been added. If the original rock is almost pure silica, the bricks may consist of silica with 1½ to 2 per cent. of lime. If the raw material is natural ganister, the bricks will also contain 2 to 5 per cent. of alumina; and if a considerable proportion of clay is used as a bond, a correspondingly larger percentage of alumina will be found in the bricks. Owing to the wide variations in the composition of the materials used, it is impossible to give a single figure which may be regarded as the average composition, though the majority of silica bricks will show on analysis: 95 to 98 per cent. of silica, 0·50 to 2·75 of alumina, 0·3 to 1·25 of oxide of iron, and 0·2 to 2·7 of lime, the proportion of the last named being usually from 1 to 2·5 per cent. Alumina is an undesirable constituent of silica bricks if more than 3 per cent. is present; lesser proportions are unimportant.

The iron in silica bricks occurs chiefly as ferrous ortho-silicate, known in nature as fayalite. Magnetite may also occur in dark masses, or as dendritic crystals. Iron compounds in small proportions do not seem to have a very serious effect upon silica bricks, but, as a rule, the iron compounds should not exceed 1·5 per cent. The principal objection to iron compounds is that they discolour the bricks. An excess of iron oxide is particularly injurious where there is over 2 per cent. of lime, as, in such cases, the refractoriness of the bricks is appreciably lowered.

The presence of a small proportion of impurity is in some ways an advantage, as it tends to increase the rate of inversion of quartz to tridymite, and to effect it at a lower temperature than would otherwise be required. Thus, red iron oxide increases the rate at which tridymite is formed and other iron compounds have a similar action.

Chemical analysis alone is useless in determining the value of a silica brick, as some of the purest silica rocks are unsuitable for brick-making on account of their continuous expansion when in use.

The following figures are fairly typical of good silica and ganister bricks, but bricks made from the same seam often vary greatly in composition:—

TABLE LXXI.—ANALYSES OF SILICA BRICKS.

Material.	Silica.	Alumina.	Iron Oxide.	Lime.	Magnesia.	Potash and Soda.
Ganister bricks :—						
Lowood . . .	96	1	0·7	1·8	0·2	0·3
Witton . . .	94	1	1	2·3	0·3	0·3
Weardale . . .	95·5	0·6	0·7	1·6	0·4	1·2
Dinas bricks :—						
Wales . . .	96	0·5	0·3	3	0·2	..

Mineralogically, silica bricks consist of cristobalite, tridymite, and a little quartz, together with about 15–18 per cent. of a glassy bond or matrix which surrounds and unites the crystalline grains (see p. 444).

The *mechanical strength* of silica bricks is largely dependent upon the composition of the raw material and the manner in which it is prepared for use, and it is necessary to exercise great care in the grinding of the rock and in its admixture with the water and lime, so as to secure a thoroughly homogeneous paste. The mechanical strength of silica bricks is less than that of fireclay bricks, and varies from 900 to 3700 lbs. per square inch, the average being 1800 to 2800 lbs. per square inch. The Institution of Gas Engineers demands in its specification that silica bricks shall withstand a crushing stress of not less than 1800 lbs. per square inch when applied to whole bricks placed on end in a machine giving a vertical thrust.

The strongest silica bricks are those in which there is plenty of bond well distributed, and with its full powers developed by careful and thorough firing. Some tests made by Emery and Bradshaw show that machine-made silica bricks are considerably stronger than hand-made ones.

According to Philipon, the crushing strength of silica bricks is proportional to (i) the fineness of the quartz employed, (ii) the proportion of water added to make the paste, and (iii) the proportion of bond added. Silica bricks containing a large proportion of impalpable silica are the most resistant to crushing; some composed wholly of such fine material had a crushing strength exceeding 2800 lbs. per square inch. The crushing strength of well-made bricks containing between 1 and 2 per cent. of lime is fairly constant, but when a greater percentage of lime is present, the strength is liable to be reduced.

The strength of refractory materials at high temperatures depends less on the chemical composition than on their physical constitution and the mode of manufacture.

G. H. Brown found that silica bricks heated to a high temperature under a slight load (*e.g.* 50 lbs. per square inch at 1350° C. to 1470° C.) will not collapse like a fireclay brick, but whereas under a greater load (say 75 lbs. per square inch) at the same temperature fireclay bricks will give way gradually, silica bricks will collapse rapidly when once the softening-point under the given conditions has been reached.

K. Endell[1] has tested silica bricks, having a refractoriness of 1750° C., which did not soften under load below 1650° C. The following table shows the results of tests of the crushing strength of a "Star" silica brick by Le Chatelier:—[2]

TABLE LXXII.—EFFECT OF TEMPERATURE ON CRUSHING STRENGTH.

Temperature. °C.	Crushing Strength. Lbs. per Sq. In.
15	2418
520	2247
670	2133
800	1977
950	1778
1050	1707
1200	1209
1320	882
1460	711
1540	526
1600	427

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[1] *Stahl u. Eisen*, 1921, **41**, 6.

[2] *Rev. de Mét.*, June 1917.

V. Bodin found that many refractory materials, especially those of clay and silica, showed a decreased mechanical strength with an increased temperature up to about 800° C., after which the strength increased, reaching a maximum at about 1000° C. On further heating, he found the strength to be rapidly reduced, reaching zero at about 1600° C. (fig. 104).

Silica bricks containing clay suffer a slight deflection when heated to 1350° C. under a load of 50 lbs. per square inch. Fig. 86, due to K. Endell, shows the comparison of the crushing strengths of silica and other refractory bricks, from which it will be seen that silica bricks retain their strength to a higher temperature than either fireclay or magnesite bricks.

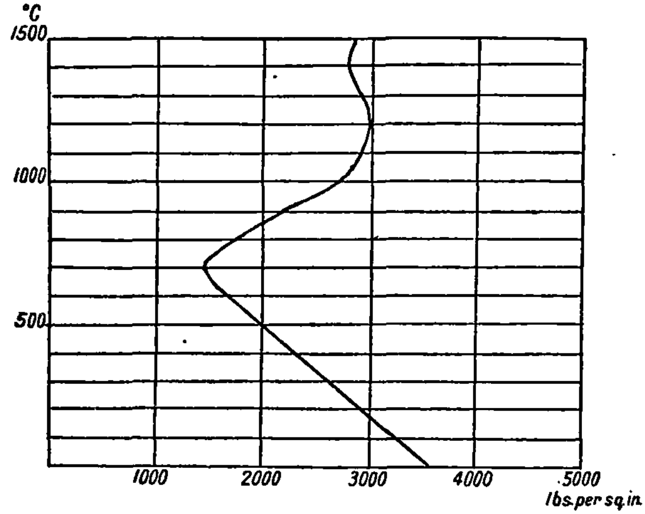

FIG. 104.—Strength of silica bricks (V. Bodin).

H. le Chatelier and B. Bogitch[1] prefer the Brinell ball test (p. 342) to the ordinary crushing test.

The *maximum working temperature* of silica bricks under load is usually about 1680° C., but higher and lower temperatures are more suitable for some silica bricks. This figure is based partly on general observations and partly on the results of determinations of the refractoriness-under-load (p. 451).

The *transverse breaking test* is a very useful one for determining the value of the binding material employed. A few bricks from each batch should be tested in this manner; the effective modulus of rupture for silica bricks of good quality should be at least 400 when cold and about 130 at 1350° C.

The *tensile strength* of silica bricks has been investigated by Chesters and Rees,[2] who used various bonds. Failure occurred with bricks in which dextrin was used as a bond, but not with sulphite lye, cellulose acetate, or clay. Silicate of soda produces a long extension before collapse and causes the silica brick to behave like one made of glass.

The **effect of heat** on silica bricks is best considered under the three headings: (i) expansion, (ii) refractoriness, and (iii) sudden changes of temperature.

(i) *Expansion.*—As explained on p. 160, the principal result of heating quartzose silica to temperatures about 800° C. is to convert it into cristobalite

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[1] *La Céramique*, 1919, **371**, 17–18.

[2] *Trans. Cer. Soc.*, 1931, **30**, 258.

or tridymite or both. This conversion into another form of silica is accompanied by an increase of more than 20 per cent. in volume and a reduction in specific gravity from 2·65 to 2·23. This means that if a brick could be made of pure quartz and be wholly converted into tridymite or cristobalite on burning, and the porosity were disregarded, it would increase in volume by 20 per cent., or ⅞ inch per linear foot. A much greater expansion may be produced by heating the bricks too rapidly in the earlier stages of burning, as this creates minute cracks and fissures.

The linear expansion does not increase regularly with the temperature, but proceeds as shown in Table LXXIII.[1] This irregular expansion tends to cause spalling and cracking.

TABLE LXXIII.

	Linear Expansion (per cent.) between		
	100° and 200° C.	200° and 300° C.	500° and 600° C.
Tridymite . . .	0·33	0·17	0·05
Cristobalite . . .	0·17	1·08	0·50
Quartz . . .	0·16	0·16	0·60

The amount of expansion which the bricks undergo on burning is a fair measure of the extent to which the conversion of the quartz has taken place. The coefficient of thermal expansion of silica bricks from 15° C. to 940° C. is, according to J. W. Mellor, about 0·0000051 inch per 1° C. per inch, whilst the coefficient from 15° C. to 1180° C. averages about 0·0000064 inch per 1° C. per inch.

The following table, due to D. W. Ross,[2] gives further details of the expansion of a silica brick on heating to 1400° C. :—

TABLE LXXIV.—EXPANSION OF SILICA BRICKS.

Temperature. °C.	Linear Expansion. Per Cent.
19	0·0
200	0·0
500	0·340
650	0·363
1200	0·408
1250	0·408
1300	0·431
1330	0·431
1360	0·657
1400	0·657
1400	0·657
1400	0·703
1400	0·840
Total expansion	0·840
Permanent expansion (after cooling)	0·158

The linear expansion of silica bricks, as compared with other firebricks,

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[1] Mellor and Green, *Chem. Ind.*, 1938, **57**, 630.

[2] U.S.A. Bureau of Standards, Tech. Paper 116.

is shown in fig. 105 (due to B. Bogitch). The irregular expansion of silica bricks is largely due to the inversions of the silica.

Silica bricks expand less when they are burned in a reducing atmosphere than in an oxidising one, because under reducing conditions ferrous silicates are formed from the iron compounds present. These silicates are readily fusible, and so fill in the interstices between the grains of silica and thereby tend to reduce the volume of the bricks as a whole on account of the fluxing effect of the iron which may be present. K. Endell[1] has suggested that silica bricks should not have a volume change exceeding 2 per cent. when heated up to 1600° C. in one and a half hours, and maintained at that temperature for half an hour. The Standard Specification of the Institution of Gas Engineers (see Appendix) allows 1 per cent. of linear expansion after heating at 1400° C. for two hours; this corresponds to 3 per cent. volume change, and is less stringent than Endell's figure.

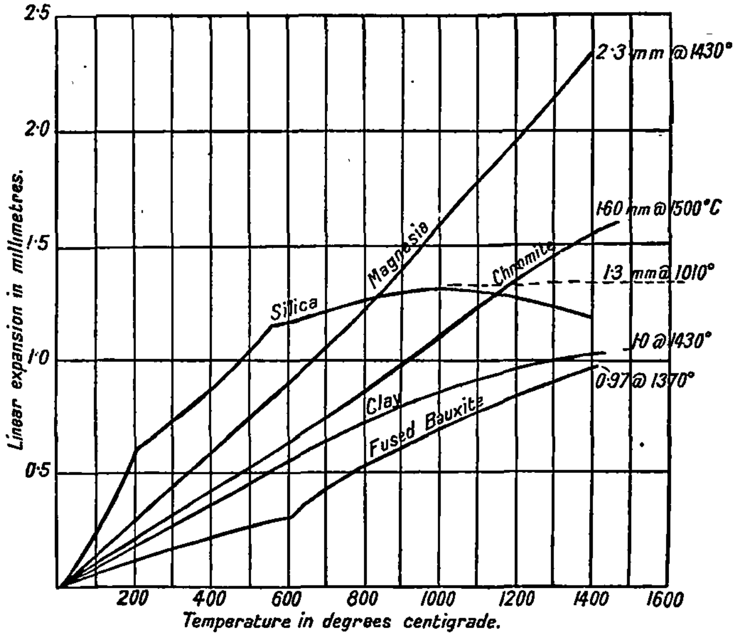

FIG. 105.—Thermal expansion of refractory materials.

The effect of the burning temperature on the expansion of silica bricks is well shown in Table LXXV., due to R. M. Howe and W. R. Kerr.[2]

Some English silica bricks are generally less constant in volume than many foreign ones, because they are not burned at a sufficiently high temperature or for a sufficiently long time. Table LXXVI., due to K. Endell,[3] shows the difference in quality.

Unless the bricks are fired for a sufficiently long time at a high enough temperature, the conversion into tridymite will be incomplete. Consequently, when the bricks are in use, they will continue to expand, and this may cause serious trouble. This is due to the fact that in the burning of silica bricks

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[1] *Journ. Amer. Cer. Soc.*, 1922, **5**, 209. [2] *Ibid.*, 164. [3] *Ibid.*, 216–217.

the conversion of quartz into cristobalite requires several days, but the conversion into tridymite requires weeks unless an accelerator is present. It is unwise to allow silica bricks to remain for a long period at 1470° C. or above because, at this temperature, tridymite loses its homogeneous structure and the bricks may crack or even crumble.

TABLE LXXV.—EFFECT OF BURNING TEMPERATURE ON EXPANSION.

Temperature of Burning. Cones.	Average Residual Expansion. Per Cent.
11	4·2
14–15	2·0
16–17	1·3
17	0·8
18	0·4
19	0·2

For most purposes for which silica bricks are used it is essential that they should not expand seriously when in use. Prior to the causes of this "growth" being discovered, it was a common cause of cracks in the brickwork with all their consequent disadvantages. It can be almost wholly prevented by burning the bricks at a sufficiently high temperature for a sufficiently long time, and when this is done the expansion on reheating to 1400°–1500° C. and cooling (after-contraction test) is reduced to less than 1 per cent.[1]

The *reversible changes* in silica bricks are those due to the expansion and contraction of the quartz, cristobalite, tridymite, and glassy matrix, each of these substances having its characteristic change.

Of these, the most important in silica bricks are those due to cristobalite and to unaltered quartz. Hence, when a new structure built of silica bricks is heated, the rise of temperature to 600° C. should be very slow, so that the expansion of the various substances may take place as steadily as possible.

The *irreversible changes* in silica bricks are those which have been effected during the manufacture. They chiefly consist of the conversion of quartz into cristobalite and tridymite. If the bricks have been imperfectly burned or if they are maintained at a sufficiently high temperature for long periods when in use, any unaltered material will tend to be inverted and a further irreversible change in volume will occur. There is also an expansion due to the devitrification of the glassy matrix, which increases rapidly above 1000° C., but ceases when the glass melts.

The formation of cristobalite and tridymite crystals tends to set up strains in the bricks which may cause cracking, as also may the solution of quartz and other forms of silica in the molten glass.

(ii) The *refractoriness* of silica bricks depends to some extent on the proportion of lime, soda, potash, and alumina present; it also depends greatly on the texture of the material (particularly on the proportion of "flour" present) and on the mode of burning. In some cases, these are of more importance than the chemical composition. The refractoriness of a mixture of pure silica and alumina is shown in fig. 29, but the lime added as a bond and the alkalies in the silica rock usually make the actual softening-point somewhat

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[1] For further information on the thermal expansion of silica bricks see pp. 163–164; and Rigby and Green, *Trans. Cer. Soc.*, 1938, **37**, 368.

lower than is shown in Seger's curve. The best silica bricks have a softening-point corresponding to Seger Cones 34 to 36 (1750° C. to 1790° C.). Pure silica begins to melt at 1600° C., but its viscosity is so great that it must be heated to 1750° C. before it flows distinctly. Some silica bricks of good reputation commence to melt at 1600° C.; many of the best-known brands, when made into the shape of Seger cones, bend over at a temperature of 1700° C. to 1730° C. (Cones 31 to 33).

TABLE LXXVI.—COMPARISON OF SILICA BRICKS.

	Specific Gravity.	Load Test. 14 lbs. per Sq. In.	Linear Expansion after Heating half an hour at 1600° C. Per Cent.	Unaltered Quartz. Per Cent.
German—				
1. Average of 8 bricks for basic open hearth furnace	2·40	1530	3·7	28
2. Average of 3 coke oven bricks	2·47	1460	4·7	32
3. Glass furnace bricks	2·47	1600	4·0	40
4. Average of 4 bricks made by German steel-works for own use.	2·34	1640	0·8	13
American—				
Medina	2·34	1620	0·5	14
Quartzite ("Star")		1535		
English—				
Ganister brick	2·40	1660 1670	3·5	22
Swedish—				
Quartzite brick	2·36	1630	2·8	16

F. Hoffmann has found that grains of tridymite $\frac{1}{25}$ inch diameter, taken from pieces of silica bricks, when observed with a low-power microscope, began to flow at 1700° C. to 1710° C., but if other portions of the same bricks were made into the shape of Seger cones, they did not bend until a temperature of 1750° C. (corresponding to Cone 34) was reached. This interesting comparison is important as showing the necessity of stating what is meant by the term "melting-point" or "softening-point" as applied to silica bricks, and also explains how several observers, employing different methods, may obtain widely different results.

When a mixture of pure silica and pure alumina is heated there is no clearly defined eutectic, but if the heating is prolonged so that mullite is formed—or, still better, if a mixture of mullite and silica is used—it will be found that the most fusible mixture (eutectic) melts at 1545° C. and contains 5·5 per cent. of alumina. Owing to this eutectic, the addition of a little alumina to some silica rocks may reduce their refractoriness, but a larger proportion of alumina makes them more refractory.

The chief lime complexes in silica bricks are: (i) a eutectic composed of lime 23·3, alumina 14·7, and silica 62·0 per cent. (m.pt. 1165° C.); (ii) anorthite, $CaO.Al_2O_3.2SiO_2$; and (iii) gehlenite, $2CaO.Al_2O_3.SiO_2$. Hence, serious difficulties may arise in silica bricks which contain both clay and lime, because of the many compounds and eutectics which may be formed. The most fusible eutectic melts at 1165° C., and if sufficient alumina is present the usual

1·5 per cent. of lime can produce 15 per cent. of the eutectic, which seriously reduces the refractoriness of the bricks. Other complexes have a similar effect, so that the proportion of alumina in silica bricks should be kept as low as possible if the conditions of use are such that high refractoriness is required.

High refractoriness in silica bricks is best obtained by the use of a material free from more than minute quantities of other oxides, especially from magnesia, potash, and soda, and by keeping the proportion of lime as low as possible consistent with the strength required for the bricks.

The smaller the proportion of lime used, the greater will be the heat resistance of the bricks. On the other hand, a very small increase in the percentage of lime present will usually add greatly to the mechanical strength of the bricks. The customary 1½ to 2 per cent. of lime is not too small to produce strong bricks, nor so large as unduly to affect their refractoriness.

Any base present will combine with the silica, forming a silicate or alumino-silicate of much lower melting-point. In silica bricks made with a lime bond, various calcium silicates and alumino-silicates are present which melt at 1170° C., but on prolonged heating they tend to form more refractory compounds which are richer in silica.

The destruction of a silica brick usually commences by a slight browning of the mass. The fine particles between the coarser fragments of quartzite coalesce, at the same time the angular shape of the particles is altered, and the colour changed from grey to white. The matrix deepens progressively in colour, and the white crystals become smaller and smaller, until they vanish entirely in the fused mass. Prolonged exposure of the latter to a high temperature, however, often causes it to become paler (grey), probably owing to the combustion of a portion of the carbonaceous colouring matter. The fused slag-like material is so complex that its chemical constitution is not fully known. It contains all the metallic oxides, combined with some of the silica, to form a fusible mass, which forms a black slag when cold.

A very important test with regard to refractoriness is the resistance of the bricks at a temperature and under a load similar to that found in an ordinary furnace or to Bleininger's and Brown's standard of 50 lbs. per square inch (see under *Mechanical Strength*).

The *volatility* of silica in the presence of carbon is greater than is commonly realised. The carbon appears to reduce the silica to the volatile silicon from which silica is again formed by reoxidation. The "volatilisation" occurs slowly at about 1750° C. and more rapidly at rather higher temperatures. In 1892, E. Cramer completely volatilised several crystals of quartz in a Deville furnace in which strongly reducing conditions prevailed. In an oxidising atmosphere with complete absence of carbon no volatilisation occurs.

The production of refractory articles made of sublimed silica (*i.e.* silica which has been "volatilised" by heating with carbon and the reoxidised silica collected in the cooler parts of the furnace) was patented by the British Thomson-Houston Co. in 1912. Their product is made by heating a mixture of 15 parts of silica, 12 parts of carbon, and 20 parts of rutile in an electric furnace under reducing conditions and collecting the sublimate. This sublimed product has an apparent density of 0·06 to 0·16, a true density of about 2·56, a flaky laminated structure, and contains silicon, carbon, titanium, and oxygen.

Later in 1912, the same firm patented a method for producing a similar material by volatilising a mixture of—

4 parts of silica.
2 ,, ,, carbon.
4 ,, ,, fireclay, with or without 1 part of manganese oxide.

In this case, the sublimed product is a soft felted refractory material of low thermal conductivity.

(iii) *Sudden changes in the temperature* of silica bricks will usually produce numerous fine *cracks* which cause them to lose their strength and spall (p. 368). These cracks are often due to the conversion of quartz into tridymite or cristobalite being incomplete in the bricks, and to its occurring suddenly owing to a rapid rise in temperature such as occurs when a flame plays on the bricks. Much of this cracking can be prevented by raising the temperature of the bricks very gradually, so that the conversion may occur slowly, and by taking care to keep new silica bricks out of contact with flame. The conversion ought to be completed by the manufacturer during the burning of the bricks, but competition and the desire for low prices cause many manufacturers to finish firing the kiln before they should do so; consequently, when the bricks are put in a furnace and a higher temperature is reached than that in the kiln, the quartz is suddenly converted into tridymite or cristobalite, with a large increase in volume, and the grains are shattered.

Spalling may also be due to the reversible expansion and contraction occurring too rapidly, to the effect of slags, to the absence of provision for the expansion of the brickwork through flexibility of the particles in the brick, or as a result of the softening of the matrix. During cooling below 250° C. the inversion of the cristobalite creates stresses which crack the bricks and may cause a form of spalling.

The average loss by spalling is about 10 per cent. in the case of hand-made bricks, whilst properly made machine-made bricks seldom spall any more than hand-made ones; they are true to shape, sharp cornered, dense, and have smoother surfaces. Spalling increases with the fineness of the materials used, so that for situations where resistance to spalling is necessary, a coarse-grained brick should be employed unless other properties not possessed by such a brick are desired. It also increases with increasing density and decreasing porosity.

The tendency to spall may be reduced by repeatedly heating the bricks to 800° C. at a slow rate and then allowing them to cool slowly. This appears to favour the formation of tridymite rather than cristobalite, and it is well known that tridymite bricks do not spall so readily as those made of quartz or cristobalite.

Fortunately, the better grades of ganister—particularly those found near Sheffield—are rapidly converted into a material containing a large proportion of tridymite. This accounts for the value of this type of silica brick. When such bricks spall readily, it is usually an indication of faulty selection of material, insufficient burning, or exceptionally unfavourable conditions of use.

It must always be borne in mind, however, that silica bricks are not well adapted for use under conditions where rapid changes in temperature occur, though they are excellent where the heat is continuous and where the bricks are only exposed to hot gases and flames.

The *thermal conductivity* of silica bricks is generally regarded as higher than that of clay bricks, but Wologdine's, Dougill, Hodsman, and Cobb's, and other experiments, show a lower conductivity for silica bricks at 500° C. to 1000° C., though the difference is small and irregular (see Table XCV.). The thermal conductivity of Dinas bricks varies from about 0·0013 gram calories per cm. per second[1] at 200° C. to 0·0021 at 1200° C. It should be remembered that a thermal conductivity test on a single brick in a test-furnace is not comparable to the conductivity in actual use.

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[1] To express the conductivity in kg. calories per second, the above numbers should be multiplied by 360.

The *specific heat* is about 0·26; that of quartz at various temperatures is given in Chapter XV. The specific heat of Dinas bricks generally varies between 0·237 at 200° C. to 0·291 at 1200° C.

The *electrical resistivity* of silica bricks, as determined by three groups of investigators, is shown in Table LXXVII.

Table LXXVII.—Electrical Resistivity of Silica Bricks.
(ohm-cms.)

Temperature, ° C.	Hartmann, Sullivan, and Allen.[1]	Stansfield, M'Leod, and M'Mahon.	A. V. Henry.[2]
cold	< 125,000,000	..	..
400	..	..	82,800,000
500	..	..	11,300,000
600	..	..	2,400,000
700	..	..	775,000
800	< 2,380,000	..	300,000
900	< 765,000	..	117,000
1000	< 300,000	..	49,000
1100	< 126,000	..	25,900
1200	< 62,000	..	15,700
1300	< 30,900	9,700	11,100
1400	< 16,500	2,400	8,050
1500	< 8,420	710	5,660
1550	..	22	..

From the foregoing it will be understood that silica bricks should have the following characteristics:—

(1) Great refractoriness, corresponding to Cone 31 or above.

(2) Very high percentage of silica and low percentage of other oxides.

(3) Sufficient crushing strength.

(4) As constant a volume as possible when in use.

(5) The bricks should have been burned under such conditions that their tensile strength whilst hot is high enough to prevent spalling when the bricks are subjected to sudden changes in temperature.

Steam has a detrimental effect on silica bricks, especially in the presence of iron compounds, and care should be taken to avoid exposure to steam as far as is practicable. For some purposes for which the bricks are used this is impossible, as steam is a constituent of the gases which come in contact with the bricks.

TRIDYMITE BRICKS.

The term *tridymite bricks* should be confined to bricks made of tridymite, but it is, unfortunately, used very loosely, and some so-called tridymite bricks consist chiefly of unaltered quartzite with a very small proportion of tridymite.

Tridymite is not found in large enough quantities to be used as a raw material. It must, therefore, be made artificially by calcining quartzite (p. 422), with or without an accelerator (p. 420), until a sufficiently large proportion of tridymite has been formed. The resulting product is ground,

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[1] *Trans. Amer. Electrochemical Soc.*, 1920, **38**, 279.

[2] *J. Amer. Cer. Soc.*, 1924, **7**, 764–782.

screened, and made into bricks in the same manner as ordinary silica bricks (p. 425 *et seq.*), so that tridymite bricks may be regarded as a special kind of silica bricks.

According to Chernous,[1] by adding to silica a frit composed of soda, iron ore, and sand (so as to add 0·5 per cent. Na_2O and 1·2 per cent. Fe_2O_3) fully tridymitised bricks can be obtained under commercial conditions.

Several other Russian investigators have found that ferrous oxide greatly accelerates the production of tridymite, particularly if the material is mixed with charcoal (to ensure reduction of the iron oxide and the formation of complex ferrous silicates). Hugill and Rees [2] have confirmed this, provided the lime-content does not exceed 1·5 per cent. The lime forms calcium ferrite, which is highly reactive and a powerful accelerator.

Numerous claims for the manufacture of tridymite bricks have been patented; some of the bricks producible by the prescribed methods would contain very little tridymite. Among the more interesting patents are:

Eng. Pat. 220,603 (1923), for the production of bricks composed of 88 parts of tridymite and 12 parts of fireclay.

Eng. Pat. 366,114 (1930), for the production of " tridymite " bricks made of sand or quartzite with 2 per cent. of chalk, 1·5 per cent. of soda, and 1·5 per cent. of iron oxide, " dried, melted (*sic*), and burnt for 24 hours at Cone 15–16."

U.S.A. Pat. 1,544,433 (1925), for the production of tridymite bricks from diatomite with 1 to 3 per cent. of lime and 2 to 7 per cent. of felspar. The chief difficulty is to avoid forming cristobalite, which spalls badly (see " Dolomite Bricks," p. 487).

Brown silica bricks or Black Dinas bricks (made by adding iron oxide and charcoal so as to produce complex ferrous silicates or by adding iron-bearing slag) are much esteemed in Russia on account of their high tridymite content, but have not become popular elsewhere. They are said to last three times as long as ordinary silica bricks in open-hearth steel furnaces and to withstand much higher temperatures. They usually contain about 2·5 per cent. of iron oxide and 30 to 54 per cent. of tridymite. The specific gravity is usually 2·4 to 2·63. Such bricks should not be used for retorts or coke-ovens, as the iron tends to reduce carbon monoxide with liberation of free carbon, which destroys the bricks.

DIATOMITE BRICKS.

Diatomite—also known as *moler*, *kieselguhr*, and *Bann clay*—is a form of silica composed of the hollow skeletal remains of certain minute plants (diatoms). It is not very suitable for the manufacture of silica bricks to be used at very high temperatures because, on heating, diatomite is inverted direct to cristobalite, with a very small expansion, but on reheating the expansion is very marked. Most diatomites are too impure to be highly refractory.

Diatomite bricks are chiefly used for the manufacture of insulating bricks (see p. 395).

For further information on diatomite, see pp. 158 and 180.

UNBURNED SILICA BRICKS.

Many attempts have been made to produce silica bricks without their having to be burned prior to use, but their production does not appear to be feasible at present.

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[1] *Ogneupory*, 1936, **4**, 197.

[2] *Trans. Cer. Soc.*, 1931, **30**, 321–336.

The more important of the " unburned substitutes " for firebricks are—

(i) Silica rock cut into blocks of suitable shape and used in the construction of kilns, in a manner similar to stone blocks used in ordinary masonry. Where the temperature attained by such blocks is not excessive, they may be used satisfactorily, and large numbers of stone slabs are used as hearth-stones, flue-covers, etc. Their use is limited to temperatures well below that at which any inversion of the silica to tridymite or cristobalite can occur, and, for most stones, constant exposure to a dull red heat would prove disastrous. Stones which are specially suitable for these purposes are known as " firestones," and have been used in glass and other furnaces.

(ii) Various mixtures of lime and crushed silica rock (or sand) hardened by steam have been patented as a substitute for firebricks. Bricks or blocks are made from such a mixture by converting it into a paste with water, shaping the blocks in a press, and then subjecting them to the action of steam under pressure or of superheated steam. This process is identical with the manufacture of lime-sand bricks; its use for *refractory* silica bricks was patented by J. Horak in 1901, by G. C. Marks in 1902, and by H. A. D. Collins in 1906, but by omitting first to calcine the silica and so convert it into cristobalite or tridymite, the bricks produced were useless on account of excessive expansion. The use of " burned sand of high specific gravity " was patented by Ponton, Mosley, and Chambers in 1889, but they unfortunately chose an alkaline silicate as the bond.

The great disadvantage of such steam-heated bricks is the necessity of using 3 to 6 per cent. of lime, which greatly reduces the refractoriness of the silica, with the result that they can only be regarded as of No. 3 or inferior grade. The addition of nitre (Bovie's Swedish patent, 1901) only reduces the refractoriness of the bricks still further. Numerous patents have been granted for modifications of the lime-sand brick process, in which steam is used as the hardening agent, but none of them yield really refractory bricks, not even when crushed firebricks (grog) are substituted for sand or silica rock (Gürtler's German patent, 1916); at a dull red heat they rapidly become friable and unable to resist pressure.

(iii) Considerable quantities of quartz bricks were used in boiler settings in Central Europe some ten years ago. These bricks were made of quartz, colloidal silica (or water-glass), and lime. After being stored some time, the excess of lime was removed by soaking the bricks in dilute hydrochloric acid or hydrofluosilicic acid and afterwards washing them in water. Notwithstanding this treatment, a large proportion of soda and lime remains in the bricks, so that they do not come within the recognised definition of refractory materials, but they have proved useful in situations where only a low refractoriness is required. Common red bricks would, in most cases, have been equally satisfactory and cheaper.

Helmbach patented in Germany (1907) the addition of 2 per cent. of water-glass to the ground silica rock, but bricks made in this manner are of limited usefulness.

A very important feature of most unburned substitutes for silica bricks, is that whilst they show a moderate amount of refractoriness under ordinary conditions of this test, they give way at a much lower temperature when in actual use. This is partly due to their low refractoriness, but chiefly to their lack of mechanical strength at temperatures above 600° C. If bricks made of silica or grog and lime and hardened by steam are heated for several hours at 650° C., they usually lose most of their mechanical strength, because, by this treatment, the calcium hydrosilicate, which acts as a bond, is destroyed, and the anhydrous silicate produced has only a feeble binding power until it has been heated to about 1300° C. or above.

A further objection to the use of all unburned blocks or bricks consisting chiefly of silica, is the expansion which they undergo when in use. This expansion can only be avoided by heating the silica to about 1400° C. prior to the bricks being used, *i.e.* by burning the bricks. Some of the less refractory, steam-hardened bricks change their volume several times when in use, as they shrink at about 600° C. when losing their combined water, then swell on account of the inversion of the silica, and finally shrink as a result of partial fusion. Bricks, etc., which are subject to such changes when in use are obviously of very limited usefulness.

In short, no method has yet been found whereby the burning of silica bricks prior to use can be satisfactorily avoided, and all patented processes for substituting steam-hardening for firing are only applicable to blocks, bricks, etc., used under conditions which do not call for a truly refractory material.

A possible exception to this statement is found in some electric induction furnaces, where unburned silica bricks have seemed to be preferable to burned ones.

SEMI-SILICA BRICKS.

Semi-silica bricks are those made of a mixture of silica and some other material. The most important of these are the *clay-silica* bricks, described in Chapter II., but the following mixtures are also used for semi-silica bricks :—

(*a*) That mentioned in H. Herrenschmidt's patent (1907), and made of 35 to 65 parts of magnesia and 70 to 30 parts of silica. The mixture is fused in an electric furnace and the product is used for bricks.

(*b*) That mentioned in the Carborundum Co.'s patent (1903), being composed of equal parts of carborundum and ganister.

(*c*) In 1891, B. D. Healey patented a mixture of 6 parts of silica, 30 parts of alumina, and 10 parts of iron oxide.

The method of manufacture is the same as that for silica bricks, the proportion of silica preventing the mixture being worked like clay.

SILICATE BRICKS.

The fact that some silicates are highly refractory has raised hopes that bricks made of various artificially prepared silicates may be more refractory than those made of fireclay or silica.

The most important silicates for this purpose are olivine, talc, serpentine, and certain barium alumino-silicates.

Olivine Bricks.—Olivines, as explained on p. 232, are orthosilicates with the general formula $2RO.SiO_2$, the best-known olivines being *forsterite*[1] ($2MgO.SiO_2$) and *olivine* ($2(Mg,Fe)O.SiO_2$).

The olivine used may be a natural mineral such as dunite (p. 232) or a synthetic product (p. 233). Jacobi first suggested the use of synthetic olivine.[2] In 1925, Goldschmidt and Knudsen[3] used mixtures of talc and magnesia, and, later, of serpentine or olivine and magnesia.

Two or more materials may be mixed together, because some olivines expand when heated and some serpentines contract, so that by mixing them in suitable proportions bricks of constant volume can be obtained.[4]

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[1] Olivine bricks which consist chiefly of forsterite are often known as *forsterite bricks*.

[2] Ger. Pat. 417,360 (1934).

[3] Norweg. Pats. 45,083 (1925), 47,407 (1926).

[4] Eng. Pat. 340,487 (1928).

The methods of manufacture of artificial olivines are described on p. 233.

Olivine bricks are chiefly made by mixing olivine with an organic binder (p. 419), with finely ground magnesia, clay, or sodium silicate, or with talc and syrup (Eng. Pat. 284,576). It is not necessary to fuse the magnesia and silica in order to produce forsterite. The two oxides may be mixed with a temporary binder, such as dextrin, made into bricks and burned at 1450°–1500° C.[1] This high burning temperature is necessary because, in synthetic forsterite which has not been heated to 1400° C., any iron present is usually in the form of fayalite in solid solution in the forsterite, but above 1400° C. the fayalite is decomposed and magnesio-ferrite formed, which is much more refractory. Talc and serpentine are usually present in olivine and necessitate the addition of magnesia in order to produce a material as rich as possible in forsterite—the most stable of the olivine series. In practice, an excess of magnesia must be added so as to convert as much as possible of the silica into forsterite, the iron into magnesio-ferrite, the alumina into spinel, and any chromium into chrome spinel, and so to prevent the formation of mobile fused silicates. Moreover, by using an excess of magnesia the various desirable compounds are more quickly formed (see Eng. Pat. 283,791). When serpentine is used, it is advisable to heat the mixture to 1450° C. before making it into bricks, though this increases the cost so much that it is seldom done. The choice of material depends largely on cost. Thus, in Russia[2] synthetic forsterite bricks are made from talc and magnesite, but they are inferior to those made of pure olivine. In Germany, olivine or forsterite bricks are made chiefly of serpentine and magnesia because this enables German materials to be employed. In the British Isles it is better to use magnesite (or magnesian lime) and silica rock or to import Norwegian olivine. In the United States olivine and magnesia form the cheapest material.

When synthetic forsterite appears to be too costly to be used commercially, olivines are almost wholly used, the composition being corrected by adding magnesia.

For instance, in U.S. Pat. 1,307,197 (1915) a mixture of 83 per cent. of magnesia and 17 per cent. of a siliceous material burned at 1600° C. is specified. This corresponds to a mixture of olivine and magnesia. U.S. Pat. 1,330,263 (1918) specifies a mixture of calcined dolomite, iron compound, and silica, and U.S. Pat. 2,026,088 specifies a magnesium silicate incorporated into a forsteritic composition. It is claimed that bricks made of this substance can be used at 1600° C. In Eng. Pat. 156,447 (1921) ground magnesite is mixed with 5–10 per cent. of basic slag and fired at 1800° C. The following patents also relate to the manufacture of olivine bricks: Eng. Pats. 260,298 (1925), 284,576 (1926), 283,791 (1927), 301,547 (1927), 307,391 (1927), 340,487 (1928), 337,605 (1929), 347,486 (1930), 352,881 (1930), 373,846 (1930), 441,516 (1934), and 447,452 (1934); French Pats. (Goldschmidt) 623,573 (1926), 643,638 (1927), 721,545 (1931), 790,877 (1935), 811,237 (1936), 811,659 (1936); additions 34,049 (1929) and 37,785 (1931).

No matter what material is used as the basis of an olivine refractory material, the stability of the product at high temperatures will depend largely on the percentage of forsterite produced on heating it, as no other magnesium silicate is stable above 1560° C. Whether it is desirable to "improve" an olivine by adding magnesia is a matter for consideration: in most cases it would be better to use magnesia alone without any olivine. The fact remains that the only way to make olivine bricks satisfactorily is to ensure that they contain sufficient magnesia to convert all the magnesium silicates to forsterite,

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[1] Ger. Pat. 417,360.

[2] A. S. Brazilwich, *Ogneupory*, 1935, **3**, 273.

and to allow any iron compounds present to be converted into magnesioferrite ($MgO.Fe_2O_3$) and any silica into magnesium orthosilicate ($2MgO.SiO_2$) (forsterite). This is particularly necessary with olivines rich in iron, as this element hinders the formation of forsterite, and to counteract this action a large excess of magnesia must be present.

Sometimes other minerals are used in addition to olivine, *serpentine*, *talc*, and *clay* being the most commonly used. The advantage of serpentine is that a fine powder is not necessary (though about 20 per cent. must be present), as the serpentine quickly permeates the magnesite when heated.[1]

Shaping.—The bricks are usually shaped in presses under a great pressure (like magnesia bricks), but cast forsterite bricks were made by C. N. Schuette [2] in 1928 by fusing a mixture of magnesia and silica in an electric furnace and casting the molten fluid in special moulds.

Burning.—The electro-cast bricks require no burning; other olivine bricks are burned at a temperature which should not be less than 1500° C. The most refractory compound of magnesia and silica consists of 57 per cent. of magnesia and 43 per cent. of silica (*i.e.* forsterite); it melts at 1925° C. The more closely olivine bricks approach the composition of forsterite the better will be their quality. A close approximation occurs in Jacobite bricks, which are composed of 60 per cent. magnesia and 40 per cent. of silica; they are made from calcined magnesium sulphate and silica heated to 1000°–1500° C., and also by fusing the mixture electrically and casting in iron or sand moulds. The refractoriness under a load of 50 lb. per sq. in. is 1550°–1600° C. according to the purity of the material; the hardness is about 9. The resistance to slag is not high.

Properties.—Olivine bricks vary so greatly in composition and other properties that no simple summary is possible. The larger the proportion of forsterite they contain the better will be their quality, because pure forsterite has a high melting-point (1910° C.), a high refractoriness-under-load, and ample crushing strength when cold. It does not crack or spall on heating and so is a good refractory material. A typical analysis of a good olivine brick shows magnesia 57 per cent., silica 31 per cent., ferrous oxide 6 per cent. and lime 3 per cent. Bricks made wholly of natural olivine are less pure and often too poor in magnesia to be worth using.

Jorslan [3] recommends a mixture of sintered magnesia 50, alundum 25, and kaolin 50 parts, which, if fired at a sufficiently high temperature, would produce a mixture of olivine and spinel.

The fact that some magnesium silicates (*e.g.* olivines) expand whilst others contract has been claimed (Eng. Pat. 340,487) as a means of producing bricks of constant volume; a mixture of 40 parts of olivine with 60 parts of a mixture of serpentine and magnesia is specified.

The best olivine bricks have a bulk-density of 2·5, a true specific gravity of 3·2–3·4 (pure forsterite 3·26 and periclase 3·6).

The *porosity* (water absorption) is 24–28 per cent.

The *refractoriness* of forsterite is equivalent to Cone 40 (1920° C.), but that of the best forsterite bricks seldom exceeds Cone 38 (1850° C.), and many olivine bricks have a refractoriness between Cones 29 and 36 (1650° and 1785° C.) because the refractoriness of forsterite is greatly reduced by the presence of a small excess of silica.

Olivine bricks are slightly more refractory than most fireclay bricks and

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[1] Pieper, *Ber. deut. ker. Ges.*, 1937, **18**, 41.

[2] *Rept. of Invest., Dept. of Comm., Bureau of Mines*, Ser. No. 2896, 1928.

[3] *Metals and Alloys*, 1932, pp. 22–24.

rather less so than the best silica bricks and magnesia bricks, but the range of refractoriness possessed by olivine bricks from various sources is so great that no detailed comparison is possible.

Refractoriness-under-load.—Test-pieces begin to show a loss of shape at 1560°–1660° C., with collapse at 1680°–1770° C.

The *resistance to slags* is higher than that of silica, but less than that of magnesia bricks.

According to Harvey and Birch [1] slags tend to dissolve out the magnesia, leaving an iron-oxide-magnesia complex in solid solution.

Olivine bricks with a composition closely resembling forsterite are almost neutral in reaction at high temperatures, but in the presence of slag and flue-dust they can react with silica bricks and with fireclay bricks, so that it is not always safe to use them as neutral bricks. They are mildly basic.

The *mechanical strength*, or resistance to crushing, of olivine bricks is usually rather lower than that of magnesite bricks, but olivine bricks are as strong as silica bricks.

The *resistance to spalling* of olivine bricks is greater than that of magnesite bricks, but they tend to spall and crack under severe conditions.

The *thermal expansion* is less than that of magnesite bricks; the *thermal conductivity* resembles that of silica bricks and is one-third to one-half of that of magnesia bricks.

The resistance of forsterite bricks to spalling is not great and their resistance to slag is low. Forsterite is one of the few refractory materials with a greater thermal conductivity at low temperatures than at higher ones.

In the United States and in Russia forsterite bricks have been used for the arched roofs of copper-refining furnaces, where they lasted three times as long as roofs of silica bricks. Their use in the iron and steel industry has not been as satisfactory as was anticipated; they have been used in England in forging and reheating furnaces, and they are extremely resistant to the fluxing action of iron compounds, but do not resist other metallic slags satisfactorily. Olivine bricks last much longer than silica bricks in the bulkheads, end-walls, uptakes, division walls between gas and air uptakes, bridge-walls, and ports of open-hearth steel furnaces. They are destroyed by drippings from silica bricks, and so cannot be used in the front and back walls of open-hearth furnaces with silica roofs, nor in positions where they are directly in contact with slag. For further information see Greaves-Walker and Stone, *Bulletin 16, Engineering Experiment Station, North Carolina State College of Agriculture and Engineering* (1938).

Alumino-silicate Bricks are made of double silicates with the formula $RO.Al_2O_3.2SiO_2$, which are produced by heating clays or mixtures of alumina and silica with a base such as magnesia, barium oxide, or lime to a temperature 50° C. below the fusing-point. An example given by F. Singer (Eng. Pat. 282,402 *et seq.*) consists of a mixture of magnesia 10–20, alumina 33–43, and silica 40–50 parts prepared by heating to 1050° C. (see also Eng. Pat. 450,961). F. Singer [2] claims that barium alumino-silicates are specially useful refractory materials. (See also "Magnesia-clay Bricks," p. 486.)

[1] *J. Amer. Cer. Soc.*, 1935, **18**, 176–192.

[2] *Trans. Cer. Soc.*, 1936, **35**, 389–400.

CHAPTER IV.

BASIC BRICKS, INCLUDING MAGNESIA, DOLOMITE, LIME, BARYTA, SLAG, AND ZIRCONIA BRICKS.

BASIC bricks are composed principally of metallic oxides such as magnesia, lime, baryta, strontia, or a mixture of such oxides, but the term is also applied to bricks made of basic slag. Bricks made of oxides of the R_2O_3 type are not regarded as basic and are discussed in Chapters V. and VII.

It is important to observe that the purest oxides are not suitable for the manufacture of basic bricks, as these oxides do not sinter sufficiently to produce bricks of the required density and hardness, so that where only a very pure oxide is available it may be necessary to add a small proportion of oxide of iron, silica, clay, or other flux.

MAGNESIA BRICKS.

Magnesite bricks, or, more correctly, magnesia bricks, form a highly basic constructional material of great refractoriness.

The manufacture of magnesia bricks may be advantageously combined with that of silica bricks, as one engine can provide power for both plants, and both kinds of bricks can be burned in the same kiln. The preparation of the materials and the production of the bricks must be effected in separate buildings, however, as the dust from one kind of brick would spoil the other.

Uses.—Magnesia bricks are chiefly used in the iron and steel industries for lining the bottoms and the side walls (as far up as the slag is likely to reach) in furnaces working the basic (Thomas and Gilchrist) process. For this it is necessary to employ a lining of a basic character, and magnesia bricks are the best yet tried for the purpose. Magnesia is gradually replacing the dolomite formerly used and specified in the earlier patents, the magnesia being generally used in the form of bricks, whilst burned dolomite is used as a mass.

Magnesia bricks are also widely used in gas- and air-ports, and many furnaces are now being constructed with the end walls and uptakes built of magnesia bricks ; in fact, they are adopted wherever basic slag is encountered in furnaces. The bottoms and side walls of some electric furnaces and the lining of some cement kilns are also of magnesia. They are not altogether satisfactory for cement kilns, but are excellent for gold, silver, and platinum refining furnaces, and for smelting lead, antimony, and copper ores, for iron puddling furnaces, strontia, and like kilns, and generally for all furnaces in which high refractoriness is required simultaneously with great resistance to metallic oxides and slags.

Magnesia is also used as a covering for fireclay bricks. It is usually applied as a paste or wash after the bricks have been laid.

The relatively high cost of magnesia bricks is soon saved by their great durability under conditions where other (acid) firebricks are unsatisfactory.

Materials.—Magnesia firebricks are made of crushed, dead-burned magnesite, preferably that which has been partially fused in an electric furnace. The purest magnesites are not always desirable, as, in order to obtain the maximum shrinkage, they require to be burned at a temperature so high that it is difficult to attain it in a gas- or coal-fired kiln, and an electric furnace is usually (not necessarily rightly) regarded as too costly in current. Alternatively; the purer magnesites may be satisfactorily calcined if they are burned several times at a temperature of about 1500° C.; but such repeated firings are very costly. Ferruginous magnesites, on the contrary, may be fully burned at a rather lower temperature in a single firing, because iron oxide acts as a flux, forming a ferromagnesian compound which melts and increases the rate of conversion of the remaining magnesia into periclase, which is the form most stable at high temperatures and, therefore, the one required for magnesia bricks.

Prior to about 1932, the most popular magnesite bricks were made of breunnerite (p. 215), but since then bricks made of purer magnesite or of a mixture of magnesite and chromite have been found to be more suitable and are now in great demand. The purer magnesite bricks, containing up to 92 per cent. of magnesia with less than 1 per cent. of iron oxide, are much more difficult to produce, but as their tendency to spall, soften and crack is very low they are likely to be used increasingly in the future, except in so far as they are displaced by magnesia-chrome (chrome spinel bricks, p. 529).

When fully dead-burned or electrically fused and cooled, magnesite produces a mass of periclase (MgO) crystals embedded in a glassy matrix or groundmass consisting chiefly of forsterite ($2\ MgO.SiO_2$). If the magnesite is not pure the following substances can be present:—

Refractory Materials.	Glassy Matrix.
Olivines, $2RO.SiO_2$.	Calcium silicates.
Spinel, $MgO.Al_2O_3$.	Calcium aluminate.
Periclase (Mg,Fe)O.	Iron silicates.
Magnesium ferrite, $MgO.Fe_2O_3$.	Complex silicates.
	Magnesio-ferrite.

The larger the proportion of magnesia in the matrix the greater is the refractoriness, because the magnesia stiffens the glassy portion and so prevents the test-cones from bending so readily as they would if more " glass " were present. For the same reason, bricks containing a large proportion of old magnesite bricks usually appear to be more refractory than bricks made wholly of new material.

The success or failure attending the use of magnesia bricks depends chiefly on the extent to which the magnesia has been converted into periclase, so that it is essential that it should be as complete as possible.

There are four forms of " magnesite " available for magnesia bricks:

Raw magnesite shrinks excessively when heated and, therefore, must be calcined before use.

Dead-burned magnesite is that which has been heated until it does not shrink seriously when the bricks are in use (see p. 221). There is always a tendency for dead-burned magnesite to consist of an irregular mixture of sintered magnesia and insufficiently burned material. Dead-burned magnesite was, until 1932, made chiefly from breunnerite and contained 8–14 per cent.

of iron oxide, lime, and silica. More recently a purer magnesite has been preferred. The iron oxide acts as an accelerator and a flux, facilitating the production of periclase, but also reducing the fusion-point of the material.

Sintered magnesite is that which has been heated sufficiently to produce a sintered or vitrified mass. It shrinks less in use than magnesite which has not been sintered, but it is rather inferior to magnesia which has been fully fused, *e.g.* in an electric furnace. Sintered magnesite is suitable for most magnesia bricks, but for those of the best quality fused magnesia should be used.[1]

The addition of various materials to the magnesite in order to increase the strength of the bricks or to reduce the tendency to spalling tends to produce materials of the kind described under " Spinel " (p. 235), and " Olivine " (p. 232), and in the manufacture of spinel bricks (p. 508), and olivine bricks (p. 463). The addition of igneous rocks such as peridote, dionte, gabbro, dolerite, basalt, serpentine, trachite, andesite, lachylite, eurite, and rhyolite (15 per cent.) with or without a little iron ore is claimed in Eng. Pat. 193,576 (1921). The addition of talc, steatite, or other magnesium silicate is claimed in Eng. Pat. 211,944 (1922).

Konopicky in 1933 patented (Eng. Pat. 432,303) the production of a sintered ferruginous magnesia in which the proportions of the various fluxing oxides are adjusted to come within a specified part of a triangular diagram, *i.e.* silica 25–35 per cent., alumina 40–65 per cent., and lime 35–70 per cent., but this range is too wide to be of much practical value.

Fused magnesia has obvious advantages, because, if the fusion is complete, the conversion to the most stable form of magnesia must be equally complete. Until recently, fused magnesia was almost too expensive to be in great demand. It can now be prepared fairly cheaply in electric furnaces, and is worth further attention. Some electrically fused magnesia shows signs of internal strain not removable by annealing.[2]

The materials, whichever are employed, are prepared as described on p. 217 *et seq.*, and the particles are cemented together by means of a suitable bond.

Bonds.—If some of the magnesia has been very finely ground, it will, when wetted, form hydrated magnesia; in that case, no bond may be needed. Usually, however, a small proportion of some bond is used. The ones principally employed are the following:—

(*a*) *Caustic magnesia* was patented by L. Williams in 1902, but was in use in the Vietsch works in 1886. The drawback to the use of this bond is the large amount required and the great shrinkage of the bricks on burning. At one time this bond was very popular, but its use is gradually diminishing, and has been abandoned in some of the best works.

(*b*) *Clay.*—This is chiefly used for inferior bricks, and cannot be recommended. The use of clay and quicklime was patented in 1881 by H. H. Lake, and also by J. B. M. Fillon and C. L. de Capitani.

The use of a mixture of calcined magnesia 83 per cent., fireclay 17 per cent., and " a small amount of sodium silicate," was patented in 1919 (U.S.A. Pat. 1,307,197).

(*c*) *Water-glass*, which is too fusible to be really satisfactory, though it is included in many patent specifications.

(*d*) *Milk of lime*, which can only be used for magnesia containing a notable proportion of silica, and is, therefore, unavailable for the best bricks.

(*e*) *Felspar* or *fluorspar* (patented by S. Pitt in 1882), both too fusible.

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[1] The use of magnesite sintered at 1500°–1600° C. is claimed in Eng. Pat. 221,799 (1923).

[2] Chesters, Clark and Lyon, *Trans. Cer. Soc.*, 1935, **34**, 249.

(*f*) *Silica* in a finely divided state forms, on heating, a fluid magnesium silicate which produces a bond of fair quality, though the molten material is liable to be too fluid and to reduce the refractoriness under load too much to be really satisfactory. The most suitable form is *gelatinous silica,* which forms very strong bricks, but is difficult to use.

(*g*) *Boric acid* (patented by W. E. Gedge in 1887, by Rawson and Littlefield in 1900, and by H. G. Turner in 1902); *borax* (patented by J. E. Kirkpatrick in 1902).

(*h*) *Caustic soda* (patented by E. F. Althaus in 1879) and its salts have been used satisfactorily as a bond for magnesia in electric furnaces, and it has the advantage of being soluble, and, therefore, capable of more intimate admixture with the magnesia than is possible with an insoluble bond.

(*i*) *Slag,* or a mixture of slag and acid (clay, silica, etc.), or *slag wool* (patented by T. Twynam in 1916). Slags are complex silicates, and may be regarded as very impure calcium silicates; they are useful bonds, but form a moderately mobile fluid when heated to a sufficiently high temperature, and so prevent the bricks from being so refractory under a load at high temperatures as when some less mobile bonds are used. The special claim made for slag wool is that it " avoids the necessity of burning the magnesite at such high temperatures as are otherwise required." Such a statement is of doubtful value.

The use of basic slag was patented as early as 1878 (Eng. Pat. 908), also 16,096 of 1910.

The addition of slag in order to reduce spalling was first suggested in 1918 and was for some time regarded as a trade secret. It tends to form crystalline olivines, which surround the crystals of magnesia (periclase) in the brick and tend to form a very strong bond.

Olivines, like slags, are silicates (p. 232); the one chiefly used as a bond is magnesium silicate (forsterite) (see U.S. Pat. 2,026,088; Eng. Pats. 193,576, 218,720, 260,298, 441,516, and 448,276).

(*j*) *Sulphuric acid* (patented by W. E. Gedge, 1877).

(*k*) *Magnesium chloride* or *magnesium sulphate.*

(*l*) *Spinels,* including serpentine, a natural magnesium aluminate, are good, but often too impure to be satisfactory, and are better replaced by spinel-forming oxides (*m*).

(*m*) *Iron oxide, chrome iron ore,* and other natural spinel-forming oxides (patented by K. A. Mankau in 1912), form bonds which are excellent in every respect. When magnesia is mixed with 6 to 10 per cent. of such oxides and burned, they combine to form friable polybasic and polyacid spinels, which act as a solvent for the basic material and transform it into a crystalline agglomerate. Such a spinel contains a plurality of bases (*i.e.* oxides of the type RO, such as magnesia, lime, ferrous oxide, potash, and soda) and a plurality of acid-oxides (*i.e.* oxides of the type R_2O_3, such as alumina, ferric oxide, and chromium oxide), its composition corresponding to $x\text{RO}.y\text{R}_2\text{O}_3$. The iron and alumina naturally present in the Austrian magnesite are sufficient to form a spinel without any addition being necessary. *Blue billy* is a crude form of iron oxide sometimes used for this purpose.

The use of *iron oxysulphide* was patented in 1902 (Eng. Pat. 21,807).

The use of *aniline oil residues* as a source of iron oxide was patented in 1924 (Eng. Pat. 207,172).

All forms of iron oxide tend to become oxidised during the heating of the magnesite mixture, and if the temperature is sufficiently high they all form *magnesium ferrite* ($MgO.Fe_2O_3$), which then forms the bond, if the proportion of silica present is not excessive. Magnesium ferrite may be prepared separately and used as a bond, or *calcium ferrite* may be prepared and used (Eng. Pats. 394,115 and 424,741).

(*n*) *Portland cement*, intended to combine the advantages of a cement with the fluxing properties of lime and silica or their compounds.

(*o*) *Coal ash* (patented by E. V. Wagner) is a very crude and heterogeneous mixture of various oxides and silica, with some compounds of these materials. Its composition is so irregular that it is not a desirable bond for high-class firebricks.

(*p*) *Colloidal matter* other than silica (patented by E. Podszus in 1912), and consisting of finely powdered magnesia (all the particles being less than 0·05 mm. diameter) mixed with a solution of magnesium nitrate and 0·3 per cent. of nitric acid. The mixture is dialysed to separate the colloidal matter.

(*q*) *A temporary bond*, such as *tar*, *boiled linseed oil*, *fat*, *cellulose lye*, *peat*, *gelatin*, *molasses*, *sugar*, *dextrin*, *gum*, or *starch*, may be used to unite the particles until they have attained a temperature at which they will be united by the flux produced on heating them. These temporary bonds burn away in the kiln and therefore do not appreciably affect the composition of the bricks.

(*r*) *Plumbago* or *graphite* is sometimes added to the material used for making magnesia bricks. It is not really a bond, but its use increases the facility with which the material may be moulded. It also increases the heat conductivity of the bricks.

(*s*) Zircon mixed with magnesite, fused and ground to powder, forms a good bond, but raw zircon is not satisfactory.

Of these, the bonds which act as fluxes reduce the refractoriness of the magnesia, whilst those which burn out produce bricks which are somewhat deficient in mechanical strength.

The present tendency is to avoid the addition of a bond and, by careful grading (p. 471) and very great pressure, to produce bricks of such strength before burning that they can be stacked in the kiln, and to rely on the production of an inter-crystalline growth (footnote (3), p. 471) to impart the necessary strength to the burned bricks.

Preparation of the Materials.—The dead-burned magnesia is prepared from the carefully selected magnesite by heating it in a suitable kiln to an extremely high temperature, as described on pp. 217–221.

The dead-burned magnesia should have been burned at such a temperature that, on prolonged heating under the conditions in which the magnesia bricks are used, no further shrinkage or change in density occurs. Otherwise, the material is unsuitable for brickmaking.

Some of the best magnesite bricks on the market have been made of a mixture of two different magnesites, viz. one very low in iron oxide and one rather rich in it. In such bricks, thorough mixing of the materials and good grading are essential.

The highest temperature attained regularly in the burning of magnesite on a commercial scale and measured by the author is 1615° C. As periclase is the stable form of magnesia at high temperatures, the raw magnesite or the corresponding bricks ought, strictly speaking, to be burned until all the free magnesia present is converted into periclase. In practice this is not the case, the magnesite being merely sintered and the bricks fired at a temperature at which only a limited amount of periclase is produced. By the aid of an electric furnace it is not particularly difficult to convert the whole of the magnesite into periclase, but such a product has only been used during the last few years. The results are so satisfactory that it is likely to be used almost exclusively in the future, as electrical fusion is the only certain means of ensuring complete inversion.

With an increased use of electrically fused or sintered magnesite there has been a corresponding departure from the use of magnesites rich in iron compounds and of mixtures of magnesite and iron ore. For the best magnesite bricks now made, the material contains 92 per cent. or more of magnesia and less than 1 per cent. of iron oxide.

Sorting.—The dead-burned magnesia, as received, should be carefully sorted in order to remove any impurities, such as dolomite, quartz, large grains of pikrosmin (a variety of asbestos which is commonly found in native magnesia ore), glassy pieces of material (which have been formed by the magnesia and other bases present uniting with the silica, etc., to form a fusible slag), clinker or ashes and under-burned magnesia. It is important that all such undesirable materials should be separated from the material which is to be made into bricks.

Crushing.—The dead-burned magnesia and the bond should be crushed separately. The *bond* should be reduced to a fine powder, preferably in an Alsing cylinder. The *magnesia* should first be passed through a jaw-crusher, followed by an edge-runner mill or a disintegrator (hammer-mill) or a ball-mill with nickel-chrome balls. To avoid too large a proportion of fines the ball-mill may be used only for the over-size from the screens for the product of the disintegrator. The crushed material should be passed over two screens—one to remove particles larger than $\frac{1}{16}$ in. and the other to remove all fine dust,[1] as the latter is a common cause of cracks and an excess of it is very undesirable. Some dust is necessary when no other bond is used.

There is a wide difference of opinion as to what are the most suitable sizes of particles and many curious differences are specified in various patents. The average diameter[2] of the crystals in dead-burned Austrian magnesite is almost the same as that of the rounded units visible under a microscope, *i.e.* 0·06–0·08 mm.

It is usually best to separate the ground material into three grades: (i) 0·06–0·02 in., (ii) 0·02–0·005 in., and (iii) less than 0·005 in., and to use these in the ratio 60 : 10 : 30; but some manufacturers prefer equal quantities of each grade, whilst others use only two grades: (*a*) 0·06–0·04 in., and (*b*) 0·01–0·005 in. Some of the older firms use a much coarser mixture, containing 23 per cent. above 0·06 in., 50 per cent. below 0·008 in., and 27 per cent. of intermediate sizes.

The ideal grades are those which will produce the densest mixture with a minimum of compacting, though it has been contended that the densest possible mixture is less satisfactory than a slightly more porous one.

Magnetic Separation.—Dead-burned, sintered or fused magnesite is very hard, and it is therefore advisable to pass the ground material over a magnetic separator so as to remove any metallic iron. Some manufacturers apply the magnets only to the crushed material (in pieces larger than $\frac{1}{8}$ in.). It is useless to use an electro-magnet if some alloy-steels are used in the crushers, as these are not attracted by a magnet.

Proportioning.—A bond may be added in sufficient proportion to the dead-burned magnesia, but the present practice of some of the most skilled manufacturers is to omit the bond altogether.[3] When a bond is used, caustic

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[1] Surplus dust can sometimes be sold to chemical works.

[2] Chesters, Clark and Lyon, *Trans. Cer. Soc.*, 1935, **34**, 243.

[3] See section (*m*) on p. 469. Under some conditions the finest particles of magnesia appear to sublime and pass into the interstices of the mass of magnesia, where they form a crystalline bond.

or colloidal magnesia is the best to employ, the dead-burned material being mixed with 10 to 15 per cent. of its weight of caustic magnesia and water. The proportion between the two varieties of magnesia must necessarily vary with the temperatures to which they have been respectively subjected. The larger the proportion of caustic magnesia, or other bond, the easier it is to shape the material, but the greater the shrinkage of the bricks in burning. Hence, it is desirable to keep the proportion of bond as low as possible. The British Thomson-Houston Co. patented a mixture of 75 to 85 per cent. of fused recrystallised magnesia, 10 to 20 per cent. of lightly calcined magnesia, and 5 per cent. of a magnesium chloride, in the expectation that the expansion of the crystalline magnesia would be counteracted by the shrinkage of the lightly calcined magnesia and the chloride, thus preventing cracking and spalling.

The best proportions of the various sizes of particles as well as of the bonds or other ingredients (if any) must be found by trial. The aim should be to use a material composed of particles of such different sizes as to obtain the densest packing, or at least to approach it. If sufficient skill is used in the grading and proportioning and in the application of a suitable pressure, bricks of the best quality will be obtained.

Water.—The proportion of water required is usually between 4 and 7 per cent., but much depends on the fineness of the particles.

Mixing.—The materials and water are mixed in an open trough mixer with two sets of blades, though in some works a pan mill is preferred. The plasticity of the materials is so slight that there is little, if any, difference between the products of these two types of mixers, provided that each is allowed to do its work thoroughly. Some manufacturers, however, prefer to omit the use of a dry-grinding edge-runner mill and put a suitable charge of roughly crushed magnesia, bond (if any), and water in a pan mill, and subject it to a process of wet-grinding for 20 to 50 minutes in the belief that by this means the various substances are mixed more intimately, and that it also facilitates the combination of any free magnesia with any free silica which may be present. It is also possible that a minute proportion of the material may be reduced to the colloidal state, but for this to take place to any considerable extent much more prolonged treatment is necessary.

The efficiency of the mixing can be tested by spreading a thin layer of the mixture on a board or iron plate and viewing it with ultra-violet rays, as this shows up the distribution of the impurities.

Hydration or Souring.—Dead-burned magnesite is not suitable for brickmaking until the smallest particles have been hydrated. For this, time is required, though not so long as is often supposed. If the wet mixture is stored in a warm place for 3 days, that should suffice, unless the proportion of fine particles is large or the dryer is worked at too high a temperature.

Tempering.—After "souring," the mixture should be tempered on a wet pan-mill to ensure uniform distribution of the moisture, though some firms omit this second tempering.

It is very desirable that the volume-weight or apparent density of the powder should be determined at this stage, so that the mixture sent to the presses may be as uniform as possible. A simple method of doing this is to press a bottomless box (measuring 3 inches by 3 inches by 3 inches, with a stirrup-shaped handle made of sheet iron) into a sufficiently large mass of the material until the box is quite full. A piece of sheet iron is then pushed horizontally through the paste, below the bottom of the box, and then lifting the box and sheet out together. With a little trimming and care the contents of the box and no more can be transferred to a pair of scales and weighed. The weight in ounces multiplied by 64 gives the volume-weight in pounds per cubic foot. Various refinements of this method may be used, but care should be taken to use a sufficiently large sample.

The volume-weight gives an indication of the amount of shrinkage which is likely to occur, and its determination enables the manufacturer to make a uniform product by mixing several batches of magnesia together, so as to form a material with a definite volume-weight.

Pressing.—The damp powder is next pressed into bricks[1] in a power-driven press similar to that shown in figs. 51 to 53, but any press suitable for making bricks by the semi-dry process may be used.

Magnesia bricks may be made quite satisfactorily in a press with a rotary table. The material in the form of a lean paste falls into one of the moulds on the table, is pressed, and the brick lifted out of the mould as described on p. 285.

The pressure required varies with the nature of the magnesia of which the bricks are made; if it is easily fusible, with a specific gravity of about 3·4, and containing grains of all sizes up to $\frac{1}{16}$ inch in diameter, a pressure of 3550 lbs. per square inch will suffice, but for a more refractory and finer brick a pressure of 10,000 lb. per sq. in. or 200 tons per brick is necessary; in some cases, twice this pressure is employed. Fitzgerald[2] has found that properly graded bricks made under a pressure of 10,000 lb. per sq. in. do not shrink, and that such bricks when unburned have greater mechanical strength and resistance to burning than burned bricks. The use of unburned bricks, suggested in 1931 by Chesters and Rees, is now usual in some electrical furnaces.[3]

The wear and tear on the die-boxes and plungers is very great, and a sufficient number of spare lining plates made of hard steel must, therefore, be kept in hand. They must usually be renewed after making 4000 to 5000 bricks, but those made of special chrome steel or of special alloy tool steel last much longer.

In order that the bricks may be as uniform as possible in size, some Continental manufacturers weigh out the material before feeding it into the die-box of the press. British manufacturers have, hitherto, regarded this as an unnecessary refinement.

Magnesia bricks tend, during burning, to shrink more in a perpendicular than in a horizontal direction. This difference, being due to the weight of the bricks, should be allowed for when making the mould or press-box. The additional allowance is about $\frac{1}{8}$ inch per foot.

Fused magnesite may be poured into moulds and then subjected to pressure (Eng. Pat. 278,120, 1926).

It has been found best to make magnesia bricks without any brand; the impression of the brand is a source of weakness which leads to cracking.

Drying.—When the bricks come from the press they should be placed on racks and dried in a well-ventilated shed without heat, though steam pipes may be used during the winter months. Magnesia bricks vary greatly as regards their tendency to crack during drying, and each manufacturer must, therefore, ascertain by trial what conditions of heating are applicable to his bricks.

The cracking of bricks during drying is chiefly due to excessive hydration

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[1] N. E. Maccalum (Eng. Pat. 10,598, 1914) claims to have obtained remarkably satisfactory results by using a mixture of raw magnesite and 10 per cent. of iron oxide which has been lightly burned, crushed to powder, dampened, and rammed into cases made of sheet iron or steel of 18 to 20 gauge, electro-welded about the joints and with both ends open. These cased bricks or blocks are laid in magnesia mortar in the ordinary manner in building open-hearth furnaces. The reason for the durability of these iron-cased bricks is not clear.

[2] *Metals and Alloys*, 1932, **3**, 25.

[3] See also *Trans. Cer. Soc.*, 1932, **31**, 243; 1937, **36**, 57–122.

caused by: (i) insufficient souring before pressing, (ii) too wet a mixture, (iii) too much fine dust in the mixture, and (iv) too hot a dryer.

Drying usually requires three weeks or more, but with a carefully controlled humidity and temperature in a closed dryer this time may be reduced to less than a week.

Chesters and Weyl[1] have found that the most rapid drying occurs at 85°–100° C., and it is then that the greatest risk of cracking occurs, accompanied by a large expansion due to the formation of magnesium hydroxide (*brucite*). Slow drying at a low temperature (20°–25° C.) appears to be essential. The most rapid expansion is at 85°–95° C.

Steam-heated floors and tunnel dryers are seldom satisfactory for magnesia bricks, as they dry the bricks too rapidly.

If magnesia bricks are kept in a warm, *moist* atmosphere for some time, they can afterwards be dried more rapidly and at a higher temperature, with very little tendency to crack. The importance of this has not been recognised by most manufacturers of magnesia bricks.

Taking to the Kiln.—Great care is needed in moving the unburned bricks, as they are very sensitive to slight shocks.

Setting in Kiln.—Magnesia bricks are very frequently burned simultaneously with silica bricks, as both require the same temperature in the kiln.[2] Each kind of brick should, however, be kept separate, *e.g.* by setting the lower part of the kiln with silica bricks and the upper part with magnesia bricks. This will reduce the number of bricks of different kinds which are in contact with each other: an important matter, as magnesia and silica react on each other to some extent and reduce each other's heat resistance. It is best to set magnesia bricks " on end " as far as possible.

Magnesia bricks can also be burned in " cupboards " or " boxes " built of other bricks, and in this way the magnesia bricks are set only two or three courses high.

The bricks should be set $\frac{3}{8}$ to $\frac{3}{4}$ inch apart—preferably the latter—so as to allow plenty of room for the hot gases to play around them.

Care must be taken that the bricks do not come into direct contact with flames. This is best effected by surrounding the magnesia bricks with silica bricks kept for this purpose and, therefore, used repeatedly.

It is not usual to burn more than 3000 magnesia bricks in a kiln or chamber, the remaining space being usually occupied by silica bricks.

The Seger cones used to indicate the progress of the burning should be mounted on pieces of previously burned magnesia brick by means of crushed silica rock or china clay made into a stiff paste with water.

Owing to the tenderness of the unfired bricks, a skilled setter should be employed to place them in the kilns, and he should be instructed to bed each brick carefully in magnesia sand. This " sand " must have been freed from dust before use, the most suitable-sized grains being about $\frac{1}{32}$ inch diameter. Fine dust causes the bricks to adhere to each other during firing. Sawdust is sometimes used instead of magnesia sand.

Special care is needed to ensure the bricks being placed uniformly, as any irregularity in the way they rest on each other will cause twisting or cracking.

The reason that magnesia bricks require very careful setting is that they are very friable. Those made under great pressure are much stronger, but also need great care.

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[1] *Trans. Cer. Soc.*, 1932, **32**, 201.

[2] This is a widespread custom in Great Britain, but it is, nevertheless, incorrect. The maximum temperature should be higher than that usually reached in silica brick kilns.

Burning.[1]—The method of burning and cooling is similar to that of silica bricks, and similar kilns are used. The kiln shown in fig. 58 has been found to be particularly suitable for the best magnesia bricks, though a continuous chamber kiln is more economical in fuel. As the bricks must be cooled very slowly, there should be at least twenty chambers, each holding not more than 10 to 12 tons of bricks. Small, low chambers are regarded as essential on account of the high temperature required and the softening of the bricks.

When possible, the sole, inner walls and arches should be built of magnesia bricks, and in other cases the kiln should be lined with magnesia bricks.

A tunnel-kiln can be used with advantage, provided that it has a sufficiently long cooling zone. Thus, at the works of Canadian Refractories, Ltd., Kilman, Quebec, an oil-fired tunnel-kiln 88 ft. long is used to produce 1000 bricks in 24 hours; the total time of burning is 40–70 hours and the maximum temperature reached is 1510° C.

The progress of the burning may be watched by means of Seger cones, but the simultaneous use of a Féry radiation pyrometer is a great advantage, as it provides a record of any falls in temperature which may occur. There should also be several spy-holes covered with mica sheet through which the burner may glance without opening the kiln.

The finishing temperatures for magnesia bricks correspond to Seger Cones 11 to 12 for bricks rich in iron, and Cones 17 to 18 for the best magnesia bricks; the higher the finishing temperature the better will be the quality of the bricks, as it is almost impossible to overheat magnesia bricks during manufacture. A number of German manufacturers heat the bricks until Seger Cone 26 (1580° C.) has bent down, and the Société des Travaux Publics et Communaux, which is the chief brick-manufacturing firm in Eubœa, have stated that they burn all their bricks in a Mendheim gas-fired kiln at Seger Cone 35. Prolonged heating (*i.e.* a long "soaking" period) is necessary when the highest temperature is reached in order to secure the maximum contraction of the mass.

The total time of firing is about twenty-four hours; the fuel consumption is 30 to 40 per cent. of the weight of the bricks.

Prolonging the firing at 1400° C. has no effect on the strength of the bricks when cold, but prolonged firing at 1500° C. is very beneficial.

Excessive heating tends to produce bricks which are too rigid and fail through lack of elasticity when in use. Apart from excessive heating, increasing the shaping pressure and the firing temperature or the period of heating reduces the thermal expansion and the risk of loss by spalling.

In well-burned magnesia bricks the iron is all present as magnesium ferrite, $MgO.Fe_2O_3$, which remains as a residue on dissolving the periclase in a solution of ammonium chloride.

The kiln-shrinkage of magnesia bricks should not exceed $\frac{1}{8}$ inch per foot; a greater shrinkage shows that the magnesite has not been burned sufficiently before being made into bricks.

Sorting.—The bricks must be carefully sorted according to size, thickness, and regularity of shape, as it is of great importance that they should be laid in the furnace with the thinnest possible joints. This is the more necessary, as magnesia bricks are too hard for them to be cut to shape without a very wasteful expenditure of time, though they can be "finished" by grinding.

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[1] As the burning is a costly part of the manufacture, several Continental firms have placed the freshly made bricks in an autoclave heated with steam at 120 lbs. pressure. This hydrates a portion of the magnesia and makes hard bricks of considerable strength. These are sold in an unburned state, but the shrinkage they undergo in use is so great that they are not likely to replace well-burned bricks, except in a few special cases.

Properties.[1]—Magnesia bricks are usually grey or dark brown in colour, the latter being due to the iron oxide present. Some bricks are white with a few brown flecks.

The *weight* of magnesia bricks depends largely on the mode of manufacture, but usually averages about 9·5 to 10 lbs. for the standard size of brick.

The *value* of magnesia bricks is chiefly due to their basic properties, combined with a high refractoriness.

The *texture* of magnesia bricks is generally that of a moderately coarse dense mass. When struck, well-burned magnesia bricks emit a clear ringing sound.

Two forms of magnesia occur in the bricks, namely, *amorphous magnesia* (specific gravity 3·0 to 3·2) and periclase (specific gravity 3·4 to 3·6). This is due to the fact that amorphous magnesia is first formed and is very slowly changed into periclase when heated to a temperature above 1200° C. In practice, it is necessary to burn the raw material or the bricks at a much higher temperature in order to secure the complete conversion of the magnesite, a temperature of 1450° C. to 1700° C. being necessary according to the nature of the material and the size of the pieces. Very small quantities of magnesite can be converted into periclase at a much lower temperature than larger ones, as the heat penetrates the latter so very slowly. In bricks containing much lime and silica, the polygonal shape of the periclase crystals is largely destroyed, the grains being rounded and set in a matrix of impurities. The rate at which the change takes place is increased in the presence of certain impurities, such as iron oxide, which combine with the magnesia and form a molten slag having a powerful solvent action on the unaltered magnesia and result in its rapid conversion into the denser form equivalent to amorphous periclase. The conversion is naturally more rapid when the impurities are uniformly distributed through the mass than where they are not in such intimate contact. It is advantageous to have as much as possible of the magnesia converted into periclase, as the latter is fully shrunk and so will not change in volume during any later heating. A well-burned magnesia brick should contain most of the free magnesia in the form of β-periclase. The silica is usually combined as forsterite and the iron as spinel.

Magnesia bricks also contain various compounds of magnesia with other oxides, the most important being (i) *magnesium ferrite* ($MgO.Fe_2O_3$), which is a dark-coloured, brown or black compound first detected in magnesia bricks by F. Cornu and confirmed by Cronshaw, and (ii) *forsterite*, a magnesium silicate ($2MgO.SiO_2$), which is formed (usually at a temperature above 1500° C.) when silica is present. According to Kowalke and Hougen, the forsterite crystals completely enclose the periclase crystals, binding them firmly together and so forming a very strong mass. For this reason, Continental users attach much importance to the presence of at least 5 per cent. of silica, and when less than this proportion is present some manufacturers add an equivalent amount of clay. A. Scott has reported the occurrence of a substance similar to the mineral monticellite ($MgCaSiO_4$) in some British magnesite bricks. The other impurities in magnesia bricks are similar to those in fireclay and silica bricks.

The *bond* in magnesite bricks is not formed by intercrystallisation of the particles, but consists of a glassy matrix, containing the greater part of the impurities, which surrounds and unites the rounded crystals of periclase. In the purest bricks the bond consists almost wholly of forsterite ($2MgO.SiO_2$).

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[1] It is very important to observe that numerous cases of poor behaviour, spalling, rapid corrosion by slag, etc., which have found their way into technical literature, are almost entirely due to badly made bricks.

Bricks made of pure magnesia are more durable than those of impure (ferruginous) magnesia, *but only if the pure material has been fully* shrunk.

Chemical Composition.—This depends on the bond (if any) as well as on the magnesite. The following are typical analyses:—

TABLE LXXVIII.—ANALYSES OF MAGNESIA BRICKS.

	Vietsch Bricks.	English Bricks of Greek Magnesite.	
Magnesia	85·31	94·74	91·86
Alumina	1·03	2·67	1·95
Iron oxide	8·02	trace	trace
Manganese oxide	0·52	..	..
Lime	trace	0·60	0·92
Silica[1]	5·01	1·53	4·68
Loss on ignition	..	0·24	0·22
	99·89	99·78	99·63

Magnesia bricks should not contain more than 3·5 per cent. of silica and 3 per cent. of lime. Silica reduces the refractoriness of magnesia bricks in an irregular manner, *i.e.* not in proportion to the silica present, silica in excess of 60 per cent. having no more effect than this proportion.

Free lime in magnesia bricks is very objectionable (see "Dolomite Bricks," p. 487), but magnesite containing about 7 per cent. of ferric oxide and 15 per cent. of lime can be made resistant to moisture and carbon dioxide by burning (sintering) it in a rotary kiln, because the particles are thereby coated with lime-iron silicates.

The *specific gravity* varies from 3·05 to 3·58, according to the extent to which they have been burned and the amount of impurities present.

In the best bricks the specific gravity should not be less than 3·48.

The *apparent density* is usually between 2·6 and 2·75.

Hardness.—The hardness of magnesia bricks is 4–5 on Mohs' scale.

Refractoriness.—Although the most fusible mixture of magnesia and silica (containing 65 per cent. of silica) melts at 1543° C., so small a proportion is usually present that no signs of fusion are normally recognisable when magnesia bricks are at this temperature unless pressure is applied (see "Refractorines-under-load"). Moreover, the melting-point of pure magnesia is so high (2800° C.) that the presence of relatively large proportions (15 per cent.) of impurities does not reduce the refractoriness of the material to below a useful level (2150° C.), so that without a load, well-made magnesia bricks should not begin to lose shape at a temperature below 2000° C. (Seger Cone 40), and the best qualities will usually stand a temperature of 2150° C. for two hours. This is considerably below the melting-point of pure magnesia (2500° C.), and is due to the impurities present in the natural magnesite. Pure magnesia is extremely difficult to use, as it will not sinter and form strong bricks at temperatures attainable in large kilns.

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[1] The difference between English and Austrian bricks as regards silica and iron oxide contents is important.

The following figures[1] show the effect of impurities on the refractoriness :-

Pure Magnesia.	Refractoriness, ° C.
+ 5 per cent. alumina	1242
+ 5 per cent. silica	1398
+ 5 per cent. silica and 5 per cent. lime	1339
+ 5 per cent. silica and 5 per cent. ferric oxide	1376
+10 per cent. ferric oxide	1390
+ 5 per cent. ferric oxide	1455
+ 2·5 per cent. ferric oxide and 7·5 per cent. lime	1512

The chief constituent of magnesia bricks (periclase) has so high a melting-point (2800° C.) that a determination of the refractoriness is not a criterion of the quality of magnesia bricks. The refractoriness-under-load is a much better indicator.

Refractoriness-under-load.—Magnesia bricks, under a pressure of 1 kg. per sq. cm., were found by K. Endell[2] to begin to soften at 1550° C. on account of the bond. A cylinder 50 mm. high was reduced to 10 mm. in 4¾ hours between 1500° and 1650° C. Some magnesite bricks become plastic when heated under pressure, but at 1450°–1550° C. they fail suddenly through shear and not gradually like fireclay bricks. This is much lower than the temperature at which they fail when in use. The difference is due to the fact that in the test the bricks are exposed on all sides, whereas in use they are supported on all sides except the face. Consequently a low refractoriness-under-load should not necessarily cause a brick to be condemned.

On prolonged use in the bottoms of open-hearth furnaces, the periclase (MgO) in magnesia bricks absorbs large amounts of iron oxide in the form of a solid solution. The grains of periclase unite and the silicates present form scattered aggregates often surrounded by periclase crystals.

The fusion in magnesia bricks when in use occurs chiefly in the compound of ferrous oxide and magnesia formed under reducing conditions and in the " solid solutions " of magnesio-ferrite (see also " Mechanical Strength ").

Maximum Working Temperature.—Magnesite bricks fail under load at 1400°–1500° C., but as the failure is always due to shearing and not to plastic deformation, the safe working temperature will depend largely on the extent to which stresses are avoided by skilful designing of the furnace. Under favourable conditions such bricks can be used up to 2000° C.

The best magnesia bricks are more refractory than fireclay or silica bricks (Cone 30 to 35), and are equally or even more refractory than chromite bricks. According to Donald, magnesia bricks commence to volatilise at temperatures between 1800° C. and 2000° C. on account of the impurities usually present, though in practice such volatilisation is so slight that it can seldom be serious.

Repeated heating in a clean atmosphere has no appreciable effect on well-made magnesia bricks, no marked tendency to crystallisation having been observed.

The *heat conductivity* of magnesia bricks is shown in the tables on pp. 372 to 374, and the *diffusivity* in Table XCV. (Chapter XIV.). Each of these properties is in favour of the rapid heating of material contained in vessels made of magnesia and of maintaining them for an indefinite time with a minimum consumption of fuel. In comparison with the corresponding figures for fireclay and silica bricks those given for magnesia are very striking.

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[1] Longchambon and Ko-Fuh-Tsiang, *Rev. Mat. de Constr.*, 1931, pp. 186B–188B.

[2] *Stahl u. Eisen*, 1921, **41**, 6.

A peculiarity about the thermal conductivity of magnesia bricks is that it gradually diminishes as the temperature increases, whereas that of silica and fireclay bricks is the reverse. Most investigators find that the conductivity (in c.g.s. units) drops from 0·013 at 200° C. to 0·008 at 1400° C., but Dougill, Hodsman and Cobb found that above 1000°C. the conductivity rises again and at 1300° C. reaches 0·095.

The *specific heat* of magnesia bricks is very high compared with that of fireclay bricks. According to E. Heyne the average specific heat between 29° C. and 1300° C. is 0·291, but Y. Tadokoro[1] found that it varies from 0·223 at 218° C. to 0·263 at 894° C., whilst Green[2] found that at 600° C. it is 0·265 and at 1115° C. 0·292.

The *electrical resistivity* of magnesia bricks is very important, as their principal use is in electric furnaces. At various temperatures, according to Hartmann, Sullivan and Allen,[3] Stansfield, M'Leod and M'Mahon, H. E. White,[4] A. V. Henny,[5] and O. A. Hougen,[6] the resistivity is as follows :—

TABLE LXXIX.—ELECTRICAL RESISTIVITY OF MAGNESIA BRICKS (OHM–CMS.).

Temperature, ° C.	Hartmann and Co-workers.	Stansfield and Co-workers.	White (500°–700° C.). Henny (800°–1500° C.).	Hougen.
Cold	< 137,000,000	..	..	..
500	..	..	100,000,000	..
600	..	..	85,470,000	..
700	..	..	32,200,000	..
800	< 5,000,000	..	33,000,000	..
900	< 240,000	..	11,600,000	..
1000	< 708,000	..	4,800,000	..
1100	< 560,000	..	848,100	..
1200	< 193,000	..	94,700	..
1300	< 67,400	86,200	14,100	6,200
1400	< 22,400	..	2,790	420
1500	< 2,500	..	615	55
1550	..	30	..	..

Chemical Reaction.—Magnesia bricks are essentially basic in character, though if well burned they are so dense and hard that a short heating in contact with acids such as silica or clay will not seriously corrode them. If the magnesia bricks are porous or are crushed before being heated with the acid, they are readily attacked, the product melting at 1600° C. (Seger Cone 24) or at a lower temperature. It is, therefore, desirable to avoid contact between magnesia bricks and fireclay or silica bricks at very high temperatures. This is usually accomplished by inserting an intermediate course of chromite or graphite bricks when constructing a furnace. The reaction between magnesia bricks and silica bricks is not so rapid as the action between magnesia bricks and fireclay bricks. According to Bischof, fireclay begins to attack magnesia bricks seriously at about 1600° C., forming a fluid grey slag. M'Dowell and Howe found that in magnesia bricks containing 3 per cent. of

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[1] *Sci. Rep. Tôhoku Imp. Univ.*, 1921, **10**, 339–410.
[2] *Trans. Cer. Soc.*, 1922–23, **22**, 393.
[3] *Trans. Amer. Electrochem. Soc.*, 1920, **38**, 279.
[4] *J. Amer. Cer. Soc.*, 1932, **15**, 598–1610.
[5] *J. Amer. Cer. Soc.*, 1924, **7**, 764.
[6] *Ind. Eng. Chem.*, 1937, **29**, 805.

lime, the reaction takes place at about 1530° C., whilst silica bricks interact at about 1610° C.; in bricks containing more lime, the reaction takes place at a lower temperature. Several firms have found, however, that if the line of contact is made sufficiently high in the furnace there is no need for an intermediate course.

The material with the most corrosive action on magnesia bricks is *iron oxide*, which is much more powerful in this respect than silica, alumina, or phosphoric acid. Hence, magnesia bricks should not be used in those parts of a furnace which come into contact with large quantities of highly heated iron oxide. The effect of iron oxide is greatly increased in the presence of phosphoric acid.

It is a curious fact that whilst lightly burned (caustic) magnesia is readily soluble in water, and especially so in water containing carbon dioxide or other acids, magnesia bricks are not appreciably attacked by these reagents, but they are soon reduced to powder by the action of *steam*, as this slakes the magnesia. The action is most noticeable when the bricks are laid in very wet cement and are heated to dry them rapidly. Many of the troubles with magnesia bricks are due to this cause.

Carbon has a peculiar action on magnesia bricks, rapidly corroding (" pitting ") any surface with which it may come in contact. The carbides of iron, nickel, and chromium, as well as siloxicon and carborundum, are even more destructive in their action on magnesia bricks. It is probable that the magnesia (MgO) is reduced by the carbon to metallic magnesium which is volatilised and so causes the " pitting." The action is said by Northrup to commence at a temperature of about 1450° C., but Kowalke and Grenfell found that it began at 1950° C. very slowly, and became much more active at 2030° C. M'Dowell and Howe found that carbon caused a loss in weight of 3·7 per cent. at 1500° C., and a loss of 27 per cent. at 2200° C.

Donald has attributed the corrosion of magnesia bricks in contact with the carbon electrodes in an electric furnace to the formation of carbides, and has stated that the resulting volatilisation, in some cases, effects the removal of half the face of the bricks. It is important to note that magnesia bricks containing much lime seem to be more greatly affected than well-burned ones containing very little lime.

Resistance to Slags.—Blast furnace slag has a very serious corrosive effect on magnesia bricks; the acid slag from open-hearth steel furnaces is much less corrosive. Basic slags have only a small effect on pure magnesia bricks, unless the slags are highly ferruginous, in which case they are more corrosive and tend to form crystals of periclase with iron in solid solution or as magnesium ferrite.[1]

Silica alone does not seriously attack magnesia; a third substance, such as alumina, lime or iron oxide, is needed even at very high temperatures, but when 20 per cent. or more of silica is present the resistance of magnesia bricks to slags is greatly reduced.

The general effect of slags is as described on p. 346, except that magnesia bricks are basic whilst fireclay bricks are acid.

The erosion due to slag is sometimes mistaken for spalling, but should be considered separately. Slag can attack the bricks and form a material of different expansion, which breaks away from the brick; this is very different from ordinary spalling.

Resistance to Abrasion.—Magnesia bricks have a very low resistance to abrasion, the purer bricks being friable and the less pure ones soft at the

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[1] F. H. Norton, *Refractories*, 1931, p. 387.

very high temperatures at which they are used. Magnesia bricks must, therefore, be laid in such a manner that they can be readily replaced when necessary.

The *mechanical strength* of magnesia bricks when cold is somewhat higher than that of ordinary firebricks, and is similar to that of well vitrified building bricks. The crushing strength usually varies from 2000 to 6000 lbs. per square inch.

The crushing strength of magnesia bricks under load at high temperatures is shown in fig. 106 (due to V. Bodin).

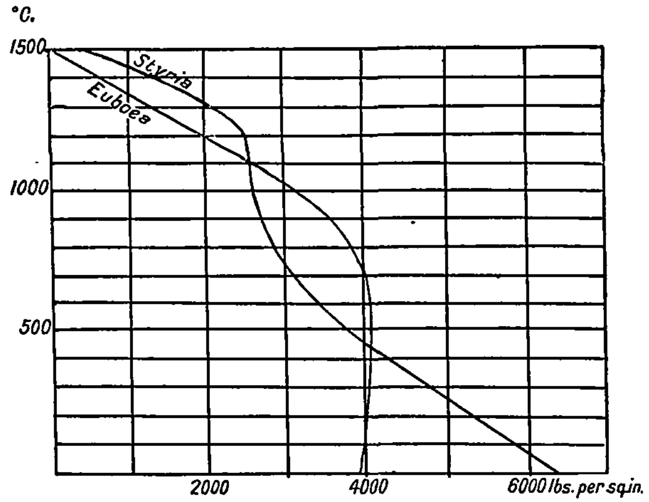

FIG. 106.—Strength of magnesia bricks (V. Bodin).

The difference in the crushing strengths of silica, fireclay, and other bricks at high temperatures is well seen in the following table, which summarises the results obtained by Le Chatelier and Bogitch :—

TABLE LXXX.—CRUSHING STRENGTHS OF BRICKS AT DIFFERENT TEMPERATURES.

Type of Brick.	Crushing Strength in lbs. per Square Inch.						
	15° C.	500° C.	1000° C.	1300° C.	1400° C.	1500° C.	1600° C.
Silica (Star brand)	2420	2135	1705	1065	855	680	425
Kaolin	2700	2560	2985	1280	(170)	(14)	(7)
Eubœan magnesia	5975	5405	4550	3840	3415	2630	(115)
Styrian magnesia	2060	1850	1210	940	(70)	(42)	(14)

The above shows very clearly the reason why silica bricks remain intact at temperatures and pressures at which other refractory materials fail. G. H. Brown has found that magnesia bricks heated to 1550° C., under a load of 50 lbs. per square inch, failed suddenly, as though a change of structure had occurred at or just below that temperature. Le Chatelier and B. Bogitch confirmed this, and suggested that it is due to the most fusible constituent in the brick melting and leaving the remainder of the mass in a condition similar to that of wet sand, so that, with a comparatively small pressure, failure occurs very rapidly.

At a temperature of 1600° C., magnesia bricks of average commercial quality are not nearly so strong as the best silica bricks, and should not generally be used under a heavy load at temperatures above 1300° C., as above this temperature they lose strength rapidly, as shown in Table LXXX. O. L. Kowalke and O. A. Hougen have investigated the reason for magnesia bricks containing silica being much stronger than those deficient in this oxide, and have found that other oxides have a similar effect, the strength, at high temperatures, of bricks made of pure magnesia being greatly increased by the addition of alumina, chromic oxide, titanium oxide, silica, or zirconia, though silica gives the most satisfactory results. They also found that bricks made of pure magnesia cannot stand a load of 66·5 lbs. per square inch at a temperature of 1680° C., whereas with the addition of 7½ per cent. of silica a temperature of 1870° C. may be reached before failure occurs.

The mechanical strength when cold may be increased by the addition of about 5 per cent. of finely ground iron oxide, but, as this acts as a flux, the strength of the intensely hot bricks is diminished by such an addition.

Heinecke has found that much stronger bricks may be made of a mixture of pure calcined alumina and dead-burned magnesia united with an organic bond. This mixture is burned at Cone 32 to a porcelain-like mass which fuses at Cone 37. The precise composition of the mixture has not been disclosed.

Porosity.—A well-burned magnesia brick for use in contact with basic slag should have a low porosity, though when such bricks are to be used under conditions where no corrosion by slag can occur, a more porous brick is desirable, as it is less sensitive to sudden changes in temperature. The porosity may be increased by adding starch, flour, cellulose, wood pulp, peat, wool, hair, or similar substances to the material used for making the bricks. The added matter burns out in the kiln and leaves pores in the bricks. Magnesia bricks, made without any of these additions, having 20 per cent. porosity, are by no means uncommon.

Volume-changes.—Well-made magnesia bricks should be almost constant in volume when in use, but they necessarily undergo the same temporary expansion as all other solids when heated. Inferior magnesia bricks, on the contrary, contract to a greater extent than the temporary expansion and so mask the latter. It is, therefore, convenient to consider the expansion and shrinkage separately.

The *expansion* of magnesia bricks in use—due to the heat—is of a wholly temporary character, the bricks resuming their former volume on cooling. This temporary expansion is about 1·9 to 1·95 per cent. up to a temperature of 1400° C. In most cases, if the temperature is raised to near that at which the bricks were burned, or on repeatedly re-heating the bricks to sufficiently high temperatures, a permanent shrinkage occurs. This is due to the fact that, under such conditions, the effect is the same as that of a prolongation of the original burning, or as if the original burning had been effected at a higher temperature. The linear expansion of magnesia bricks on heating, as determined by B. Bogitch, is shown in fig. 105. The reversible thermal expansion is high, being rather more than 2 per cent. from cold up to working temperatures.

Lynam and Rees[1] have found that the reversible expansion in magnesia bricks is proportional to the magnesia present.

The thermal expansion of electro-fused magnesite bricks is lower than that of bricks made of dead-burned magnesite, viz. 13·4 to $14{\cdot}5 \times 10^{-6}$, corresponding to 1·3–1·4 per cent. at 1000° C. The expansion differs in bricks from various sources, because the chief constituent (*periclase*) has a much larger coefficient of expansion at high temperatures than the siliceous glass which unites the crystals of periclase, with the result that the bricks spall or crack easily. This may be reduced by employing very high pressures when shaping the bricks.[2]

If the raw material has been properly dead-burned the change from amorphous magnesia to periclase in service will cause very little volume-change. Insufficiently burned material, on the contrary, will show a great contraction when in use.

Shrinkage.—Properly burned magnesia bricks which have been made from a good quality of dead-burned magnesia should not shrink greatly in use. Shrinkage is characteristic of insufficient burning. The probable extent of the shrinkage may be learned by determining the specific gravity of the bricks. Fully burned magnesia has a specific gravity of 3·5 to 3·6, whereas the incompletely burned magnesia has a specific gravity of only 3·0 to 3·4 (see p. 221). Hence, the lower the specific gravity, the greater the probable shrinkage when the bricks are used.

The greater part of the shrinkage of magnesia bricks is due to a loss of porosity caused by the drawing together of the particles by the semi-molten bond.[3] The chief shrinkage occurs at 1450° to 1500° C.

It is generally agreed that good magnesia bricks should not shrink more than 15 per cent. of their volume (or 5 per cent. of their length), and a somewhat lesser contraction is in all cases desirable. It is by no means easy to keep the contraction within the desired limits, as the influence of the varying size of the grains of clinker, variations in the pressure applied in formation, and in the temperature and heating of the kiln all exercise an influence on the density and shrinkage of the bricks.

According to T. Twynam's patents (1915) an intimate mixture of magnesite and chrome iron ore or slag wool does not shrink when burned!

Secondary shrinkages occur at about 1470° C. when alumina and chromite are present.

The addition of 2 per cent. of common salt reduces the temperature at which shrinkage occurs. That of fluorspar acts similarly.

The *thermal conductivity* of magnesite bricks diminishes from 0·015 (cold) to 0·008 cal./cm./° C./sec. at 1300° C. It is nearly double that of silica and fireclay bricks over the same range of temperature.

The *brittleness* of some magnesia bricks can be reduced by grinding the magnesia more finely and by adding 2 to 3 per cent. of felspar.

Sensitiveness to sudden changes in temperature is chiefly due to:

(i) Insufficient burning, so that too little of the magnesia is converted into periclase. By calcining and then fusing the raw magnesite, this change can be largely completed before the material is made into bricks, and the greater part of the spalling and sensitiveness to changes in temperature can then be avoided, though at a very great increase in the cost of manufacture.

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[1] *Trans. Cer. Soc.*, 1937, **36**, 137–151.

[2] For further information on the thermal expansion of magnesite see Rigby and Green, *Trans Cer. Soc.*, 1938, **37**, 382.

[3] Chesters and Parmlee, *Trans. Cer. Soc.*, 1933, **32**, 340.

Other causes of spalling are:

(ii) Too porous a material, which may cause further shrinkage. Most dense materials are much more sensitive than porous ones. If the spalling is due to the particles being too large and the mass deficient in bonding material, the defect may be minimised by grinding the material more finely, thus bringing the grains into more intimate contact with the impurities which act as catalysts and convert the amorphous magnesia into the crystalline variety much more rapidly than when pure magnesia is heated alone. Excessive grinding, however, should be avoided, as this might cause " dunting " to occur. Sometimes spalling is reduced by the application of greater pressure in shaping the bricks.

(iii) The thermal expansion of magnesia bricks being twice that of fireclay bricks, so that sudden cooling causes a very rapid contraction; if the particles are not sufficiently well cemented together the bricks will spall or crack.

(iv) Insufficient pressure applied in shaping the bricks. One of the chief means now used for minimising spalling is to apply a pressure of 200 tons per brick.

(v) Insufficient allowance for the expansion of the brickwork, the effect of slags and fluxes and unexpected movement of the brickwork.

Thermal shock is a term used to indicate various changes which occur when an article is subjected to one or more rapid changes in temperature. Hence, spalling is attributed to thermal shock, and so are several kinds of cracking. For further information on destruction due to thermal shock see " Spalling."

Spalling, or failure to withstand stresses produced by changes in temperature, is usually the result of changes in volume in different parts of the material. The chief factors concerned are (i) the reversible thermal expansion and contraction, (ii) the temperature diffusivity, and (iii) the elasticity of the various portions of the material.

Substances, like silica and magnesia, which expand irregularly through various temperature-intervals are particularly liable to spall.

Spalling is partly due to the differences in the coefficients of expansion of the magnesia and the vitrified bond, so that suitable modifications in the latter should greatly reduce the spalling.

Magnesia bricks have a relatively high thermal diffusivity, which tends to reduce spalling, but their high thermal expansion between 25° and 1200° C. tends to increase spalling.

According to Jay and Chesters[1] resistance to spalling does not depend on the size of the crystals present.

Spalling can be reduced by altering the composition of the bricks, *e.g.* by converting the magnesia into a spinel or an olivine, or both, or by making the bricks of a suitable mixture of magnesia and alumina, clay or chromite (see pp. 486–487 and 525).

The spalling of magnesia bricks has, to some extent, been overcome by the use of " Metalkase Bricks,"[2] which consist of tubes of mild steel of any convenient shape and thickness closely packed with dead-burned magnesia. These pieces are built up to form the walls, etc., of the furnace, and when the latter is in use the steel casing melts and combines with the magnesia to form a ferruginous slag which is absorbed by the bricks forming a highly resistant basic surface, the wear on which is remarkably uniform and there is scarcely any spalling.

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[1] *Trans. Cer. Soc.*, 1938, **37**, 209–230.

[2] See footnote (1) on p. 473.

Defects in Magnesia Bricks are of two chief classes—

(i) Those due to the mode of manufacture.

(ii) Those inherent in the properties of magnesia.

The first class of defects is due to causes similar to those which affect the manufacture of silica bricks and other articles which are made by compressing a powder in a mould. Air may be contained in the brick and render it fragile before firing and blistered after, if the two parts of the press which form the mould do not fit each other properly. If the edges of the mould are defective, the pressure will be, to a large extent, ineffectively applied, and the bricks will not be sufficiently firm; some lamination occurs when air is imprisoned in the die.

As already stated, the contraction of magnesia stone on firing is very great, and, consequently, if the clinker has been imperfectly fired before it is ground and pressed into bricks, the second firing will be fraught with considerable difficulty, and probably with much loss, as the bricks will lose their shape and may fall in the kiln. Even with carefully burned clinker it is necessary to guard against variations in the contraction which it may undergo during the second firing, and on this account the sorting of the clinker must be carefully carried out, and carefully chosen material fed to the grinding mill. Under-fired magnesia—whether in the form of calcined material or bricks—is sure to be defective.

The second class of defects is more difficult to control, as it concerns the inherent properties of the material and includes (*a*) spalling; (*b*) inability to withstand the corrosive action of slags; and (*c*) inability to withstand great stresses.

Spalling is probably the most important defect, as magnesia bricks are extremely sensitive to sudden changes of temperature and to the action of steam, and, when subjected to such conditions, the outer face of the brick flakes off. Spalling may be minimised—yet seldom wholly prevented—by means of the precautions mentioned on p. 484, the most important of which is to use only fully burned material.

The inability of magnesia bricks to withstand the corrosive action of basic slags with which they come into contact can only be avoided by using bricks with a dense surface so as to reduce the penetration to a minimum. The impurities and slag are absorbed into the brick through the pores and irregularities in the surface of the bricks, and chemical alterations involved take place according to the area of surface exposed, which is increased by irregularities and by pores. With very rough and porous bricks, the action at high temperatures may be so violent as to result in frothing, but with moderately smooth or dense bricks the difficulty is not often very serious.

There are seven classes of magnesite bricks on the market:

(i) Bricks made of electro-fused magnesite with little or no bond. These are the best bricks in every respect.

(ii) Bricks made of almost pure magnesite, properly dead-burned, but not necessarily electro-fused. They contain less than 1 per cent. of iron compounds, are very resistant to basic slags and have only a moderate tendency to spall.

(iii) Bricks containing a notable proportion of iron compounds. They were, at one time, the chief commercial magnesite bricks, but are now regarded as inferior to (i) and (ii) though still used in many works.

(iv) Bricks made of dead-burned magnesite with about 10 per cent. of alumina or slag. They resemble, but are superior to, (iii). (See Eng. Pat. 418,580; "Spinel Bricks," p. 508.)

(v) Bricks made of magnesite and chromite (see "Spinel Bricks," p. 508).

(vi) Bricks made of magnesite and silica or of olivine (see "Olivine Bricks," p. 462).

(vii) Bricks made of magnesite and steatite (see "Magnesia-Steatite Bricks," *below*).

MAGNESIA-SILICA BRICKS.

See "Olivine Bricks," p. 462.

MAGNESIA-STEATITE BRICKS.

These bricks resemble olivine bricks in many respects, but instead of forsterite being the chief constituent cordierite, $2MgO.2Al_2O_3.5SiO_2$, enstatite, $MgO.SiO_2$ (m.pt. 1100° C.) and clinoenstatite, $MgO.SiO_2$ (m.pt. 1200° C.) are formed. All these substances have so low a melting-point that bricks made of them can scarcely be regarded as refractory bricks.

Makhl[1] has compared the behaviour of mixtures containing talc and 58 per cent. of silica and 29 per cent. of magnesia with those containing three dunites of 31 to 35 per cent. of silica and 36 to 42 per cent. of magnesia, and concluded that the talc mixtures are all superior to the dunite ones.

Cordierite (pp. 84 and 234) when pure has the formula $2MgO.2Al_2O_3.5SiO_2$; the natural mineral commonly corresponds to $H_2O.4(Mg,Fe)O.4Al_2O_3.10SiO_2$.

α-Cordierite is pseudohexagonal and orthorhombic; stable at high temperatures.

β-Cordierite occurs as fibres; at 925° C. it is converted into the α-form.

Synthetic cordierite is formed by heating mixtures of talc, kaolin, and alumina above 1350° C. but below 1450° C., when it fuses and dissociates. A suitable mixture for synthetic cordierite consists of talc 40, clay 47, and alumina 13 parts, and this reacts more rapidly than a mixture of magnesia 13, bauxite 39, and quartz 48 parts.

The range of vitrification of cordierite is so short that it cannot be used alone as a refractory material. The range of vitrification can be greatly extended and the resistance to spalling greatly increased by adding 30 per cent. of zirconia.[2]

MAGNESIA-CLAY BRICKS.

The compounds formed by heating magnesite with china clay or kaolin can be used for making refractory bricks provided they contain less than 23 per cent. or more than 44 per cent. of magnesia[3] (see pp. 84 to 86). Bricks made of such material spall less than magnesite bricks, the minimum spalling occurring with a material corresponding to cordierite ($2MgO.2Al_2O_3.5SiO_2$).

The addition of kaolin to magnesite increases the range of plastic deformation, but seriously lowers the resistance to slag.

The effects of magnesia on clays and *vice versa* are shown on pp. 84 to 86.

Mixtures of magnesia, felspar, and clay produce a good refractory porcelain (p. 712).

MAGNESIA-ALUMINA BRICKS.

These are described under "Spinel Bricks," p. 508.

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[1] *Ker. i Steklo*, 1934, **10**, 29.

[2] Parmelee and Thurnauer, *Bull. Amer. Cer. Soc.*, 1935, **14**, 69.

[3] Cross and Rees, *Trans. Cer. Soc.*, 1934, **33**, 379–430.

MAGNESIA-CHROME BRICKS.

As chromium oxide behaves very like alumina, magnesia-chrome bricks may be regarded as a variety of spinel bricks (see p. 508).

MAGNESIA-ZIRCONIA BRICKS.

There are two fusible eutectics of magnesia and zirconia; one, containing 18 molecular per cent. of magnesia, melts at 1460° C.; and the other, containing 55 molecular per cent. of magnesia, melts at 2180° C.[1]

The compound $Mg_2Zr_3O_8$, discovered by Ruff and Ebert,[2] appears to be the most suitable constituent of magnesia-zirconia bricks.

UNBURNED MAGNESIA BRICKS.

It has been found that by using an organic substance or colloidal magnesia as a bond, magnesia bricks can be used without having previously been burned. It is essential to use a pressure of 200 tons per brick, as the bricks must be of great density. A very high pressure with a suitable bond reduces the firing shrinkage, porosity, permeability, and thermal sensitivity to such an extent that the unfired bricks can be used as satisfactorily as fired ones. This is due, according to W. J. Rees, to there being a mathematical relation between the moulding pressure and the physical properties. These unfired bricks are chiefly used in electric furnaces and rotary cement-kilns. Originally used in the United States, unburned bricks were first introduced into this country by J. H. Chesters and W. J. Rees,[3] and they are now in regular use in some works (see also p. 473).

DOLOMITE BRICKS.

Dolomite bricks are similar in many respects to those made of magnesia, though the latter are superior and, usually, are more carefully manufactured.

Dolomite bricks usually shrink greatly on burning and many of them are, therefore, unsound. They are usually porous and so soft that they wear away rapidly. Their chief interest lies in the fact that they were first used in the construction of basic linings for furnaces under the patents of Thomas and Gilchrist granted in 1879 and 1880. In recent years, they have been largely replaced by magnesia bricks.

Uses.—Dolomite bricks are used for the same purposes as magnesia bricks. They are also used for lining the kilns in which the dolomite is burned to form lime. The chief claim of the manufacturers is that magnesite does not occur in this country, but must be brought from great distances and under inconvenient conditions of transport, and as magnesium limestone can be obtained readily, " dolomite " bricks can be made more cheaply than magnesia bricks. Unfortunately, they are less durable, so that the lower first cost is largely counterbalanced by the greater frequency with which they must be renewed.

Materials.—Dolomite bricks are made of magnesian limestone which has been prepared, burned, and crushed as described on pp. 225 to 227. Usually the hardest burned (sintered) limestone is employed, but some firms prefer a

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[1] Ebert and Cohn, *Zts. anorg. allg. Chem.*, 1933, **213**, 321.

[2] *Zts. anorg. allg. Chem.*, 1929, **180**, 19.

[3] *J. Iron Steel Inst.*, 1931, **123**, 479; *Trans. Cer. Soc.*, 1932, **31**, 243

mixture of hard-burned and lightly-burned (caustic) stone. Sintered or dead-burned dolomite is used in comparatively large quantities on the Continent for lining Bessemer converters and the furnaces used in the basic open-hearth process. It is prepared by heating dolomite in the same manner as dead-burned magnesia is made from magnesite, or pieces of dolomite not larger than 3 inches diameter may be mixed with suitable coke and burned in a shaft-furnace fitted with an air-blast. The burning temperature should not be less than Cone 9 (1280° C.), and a still higher temperature is preferable.

The sintered dolomite should be carefully sorted and freed from obvious impurities. It is then crushed to pieces $\frac{1}{16}$ to $\frac{1}{4}$ inch diameter. All dust should be removed by screening.

According to Zyromsky, dolomite containing 4 per cent. of iron oxide and alumina and 2·5 per cent. of silica are the most suitable for producing the sintered product, these percentages representing the highest proportion of fluxes compatible with sufficient refractoriness.

For information on *purifying* magnesian limestone, see p. 229.

The *bonds* used in making dolomite bricks may be any of those mentioned on pp. 468 to 470, all of which have been included in various patent specifications for the manufacture of dolomite bricks. The earliest of these specifications is that of S. G. Thomas in 1876, in which the bricks are stated to be made of dolomite and clay, or dolomite alone, without a bond.

The most widely used bond is *tar*—preferably one which contains 65–75 per cent. of pitch and on coking forms a good coke.

The following additional bonds have also been used:—

Caustic lime or *quicklime*, made from either pure limestone or dolomite, and corresponding to the use of caustic magnesia for magnesia bricks. This bond is included in J. Furstenhager's patent (1880).

Magnesium silicate is generally employed in the form of *steatite*, as in Brit. Patent 3434, 1913.

Magnesium chloride, to the extent of 5 per cent., has been suggested by H. G. Schurecht, who claims that it enables very strong bricks to be obtained.

Basic slag (patented by H. E. Mason in 1910). H. G. Schurecht has shown that bricks containing basic slag are liable to disintegrate by the formation of a powder on their surface. He found that a mixture of 30 parts of basic slag and 70 parts of dolomite disintegrated in 70 days.

Iron ore or *red iron oxide* is probably the best bonding agent for dolomite bricks, especially if it is used in conjunction with an equal amount of clay; it then binds the dolomite together into a very strong mass, which does not disintegrate on repeated heating and cooling. This bond has not yet been used extensively, but so far as it has been employed it is equally as satisfactory for dolomite as for magnesia bricks.

The addition of ferrous carbonate [1] lowers the (sintering) temperature at which porosity begins to decrease and the temperature at which the maximum strength is reached. The refractoriness-under-load decreases proportionally to the increase in ferrous oxide, but all dolomite bricks have a long plastic range.

It is necessary to limit the proportion of iron oxide and silica to about 6 per cent. each, or the resultant product will be unstable.

The addition of 0·5 to 5·0 per cent. of iron oxide, chromium oxide, or alumina forms part of Eng. Pat. 440,011 (1935).

Shales and *clays* alone are not suitable bonds for dolomite bricks, as calcium orthosilicate is formed and involves an increase in volume of about 10 per cent.,

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[1] Krause and Guhr, *Feuerfest*, 1931, 7, 129.

which is sufficient to shatter dolomite bricks bonded only with clay on account of their inherent weakness.

Mixtures of dolomite and kaolin containing 50 to 75 per cent. of dolomite disintegrate after firing,[1] owing to the presence of calcium orthosilicate. Mixtures containing 80 to 90 per cent. of dolomite are more stable and have little tendency to hydrate.

A dolomite brick made of dolomite 400, silica sand 83, and lime 116 parts was patented in Canada in 1937 (Can. Pat. 358,403). The product consists of merwinite ($3CaO.MgO.SiO_2$) mixed with periclase (MgO), and is claimed to be stable in water.

Sulphate of lime or *magnesia* (patented by T. S. Gilchrist in 1880, the proportions recommended by him being 100 parts of dolomite and 60 parts of bond). *Phosphate of lime* is also recommended to reduce the shrinkage.

Acetic or *hydrochloric acid* (patented by A. von Kerperley in 1880).

Of these numerous bonds, the one which would appear to be the most satisfactory is lightly burned dolomite or quicklime, but there are peculiarly great difficulties connected with its use. Consequently, the bond most extensively used is tar or soft pitch, a by-product in the manufacture of gas from coal. H. G. Schurecht has stated that tar-bonded bricks shrink and crack less than water-bonded bricks. No one in England appears to have succeeded in making satisfactory dolomite bricks in the same manner as magnesia bricks; there is an opening for further work in this direction.

The following general statements apply to most of the mixtures of dolomite with other materials, but occasionally troublesome exceptions appear with some dolomites:—

(i) Highly aluminous fluxes produce the most stable product (dolomite-spinel bricks).

(ii) Mixtures containing fluxes rich in iron disintegrate on storage.

(iii) Fluxes rich in silica form $2CaO.SiO_2$, and the bricks tend to disintegrate on storage.

The removal of lime from burned dolomite has been described on p. 229. This is important, because the chief source of the lack of stability in dolomite bricks is the quicklime formed when dolomite is heated, and the great sensitiveness of lime to moisture. The future development of dolomite as a brickmaking material will probably involve the use of a dolomite from which most, if not all, of the lime has been removed.

Preparing the Materials.—The " dolomite " is usually reduced to a coarse powder, all of whose particles will pass through an opening $\frac{1}{4}$ inch in diameter. It should not be too fine, as this makes the bricks unduly sensitive when in use.

If both hard-burned and lightly-burned " dolomite " are to be used, the hard-burned should be quite coarse, and the lightly-burned " dolomite " should be as fine as possible. If hard-burned " dolomite " is to be used exclusively, about one-quarter of it should be ground fine enough to pass through a sieve with 100 holes per linear inch, unless tar is used as a bond, when none of the dolomite particles should be less than $\frac{1}{32}$ inch and only a few less than $\frac{1}{16}$ inch diameter.

The preliminary crushing is best effected with a stone-breaker, any further grinding necessary being done in an edge-runner mill, ball mill, or tube mill.

Proportioning.—When both hard-burned and lightly-burned dolomite are used, they should be in the proportions of 3 parts of the former to 1 part of the latter. The quantity of tar required is usually about one-tenth to

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[1] Cross and Rees, *Trans. Cer. Soc.*, 1934, **33**, 442.

one-fifth of the weight of burned dolomite. When iron oxide is used, about 5 per cent. is generally found to be suitable.

In addition to the bond an accelerator (p. 420) may be used or a substance such as slag-wool (Eng. Pat. 102,386—1916), silica, alumina, or chrome may be added so as to produce a kind of olivine or spinel brick. The great mobility of calcium silicate is, however, a sound reason for avoiding the addition of silica or materials containing it. F. E. Lathe[1] claims that if iron oxide is present and the silica is 1·4 to 4·0 times the weight of the lime a stable product is produced, which can be used for bricks for lining cement-kilns.

Mixing.—When a mineral bond is used, the various materials are mixed in the same manner as for magnesia bricks or silica bricks. With tar the dolomite is spread on a cement floor and hot tar is sprinkled over it. The materials are roughly mixed by means of spades, and the mixing is completed in an edge-runner mill with a solid revolving pan, in the same manner as when tempering clay, except that no water is used. In some cases, a vertical pug mill with a steam jacket is employed, the cylinder being about 6 feet 6 inches high and 3 feet wide.

Ageing.—H. G. Schurecht has found that it is desirable to store the wet calcined material in order to " age " it and so prevent the bricks cracking during drying. This does not apply when a tar-bond is used.

Moulding.—The bricks are moulded by hand in iron moulds, or preferably in powerful presses such as shown in figs. 51 and 53. The shaping of the bricks is, in each case, precisely similar to that used for magnesite or for carbon bricks according to the bond used. In pressing dolomite bricks, a pressure of about 10,000 lbs. per square inch or 200 tons per brick is used for bricks of the best quality, but for poorer qualities less than half this pressure is often used. One German firm claims that 400 tons per brick is used in its presses. Dolomite bricks may also be made by pouring molten dolomite into moulds, as in the casting of bricks of molten alumina (p. 511). (Eng. Pat. 340,958—1928 is void.)

Hardening.—The bricks are stored in a shed for a few days in order that they may become hard and are then sent to the kiln.

Burning.—Dolomite bricks may be used in the green state, but the shrinkage is so great that it is preferable to burn them before use. The burning may be effected in any kiln suitable for refractory materials, small down-draught or Newcastle kilns being quite suitable. If a sufficient number are to be made, a small tunnel kiln would be preferable. Tar-bound bricks are burned in the iron moulds, and should not be set more than seven courses high. When tar is the bond, the temperature is raised slowly for about eighteen hours, at the end of which time the bricks should be hot enough for the tar to coke rapidly, yet not so hot that there is any danger of explosion. As soon as the coking is complete—this can only be judged by drawing trials and by experience—the kiln is heated strongly for six to eight hours and is then closed completely, no more heating being necessary. The final temperature reached is never very high and rarely reaches Seger Cone 5*a* (1180° C.), this being one of the reasons why dolomite bricks are usually inferior to magnesia bricks.

Much better bricks are produced by using a mineral bond, such as lightly burned dolomite, quicklime, iron oxide, or a mixture of it and clay, and burning them at temperatures similar to those used for magnesia bricks, *e.g.* Seger Cone 30 (1670° C.) or above. The proportion of fuel required for burning dolomite bricks is 40 to 50 per cent. of the weight of the bricks burned. The shrinkage of the material varies from 24 to 50 per cent.

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[1] *Chem. Eng., World Power Conf.*, **B1**, 1936.

Cooling.—Dolomite bricks made with tar, as described above, only require about two days to cool; those made with a mineral bond require about a week.

Drawing the Kiln.—As the bricks are removed from the kiln they are stacked, sorted, cleaned free from any adherent matter, and are then ready for sale.

Storage.—Many attempts have been made to prevent dolomite bricks deteriorating during storage; most of these are based on (i) the exclusion of air, as by dipping the bricks in hot tar or in molten fat or wax (Eng. Pat. 191,412); (ii) conversion of any free lime present into sulphate (by dipping the bricks into a solution of a soluble sulphate); and (iii) the addition of a silicate, such as felspar, to the dolomite prior to making it into bricks (Eng. Pat. 197,791). Another method consists in packing the calcined dolomite into metal cases, each the size and shape of a brick, and coating the ends with a mixture of tar and rubber, but the cost of the casings is very great.

The action of moisture on burned dolomite is retarded, according to C. S. Garnett (Eng. Pat. 368,798—1930) by mixing it with kaolin and labradorite and re-burning. Other substances claimed as preventing hydration are silicates, olivine, talc, serpentine, bauxite, felspars, pyroxenes, and augites (Eng. Pats. 197,791—1922, 211,944—1922, and 218,720—1924). These all reduce the refractoriness.

Dolomite bricks can also be made resistant to moisture by adding a flux prior to forming the bricks. Most fluxes which have been tried are not satisfactory, but the addition of about 7 per cent. of iron oxide (calculated as ferrous oxide) and about 19 per cent. of dolomite and heating in a rotary kiln give much better results.[1] An excess of silica must be avoided, as it tends to produce a disintegrating silicate.

Fully stabilised bricks made of magnesian limestone have been made by the Refractory Brick Co. of England, Ltd., since 1936 and are being used (1939) particularly in steel-works.

Properties.—The chief properties of dolomite bricks are similar to those of magnesia bricks, described on p. 476. Dolomite bricks are, however, less strong, more porous, and, as usually supplied, shrink greatly when in use, so that they are much less durable than magnesia bricks. With the increasingly stringent demands of the iron and steel industries, and after much research, a method has recently been found for using magnesian limestone (which is abundant in England) instead of magnesite for making basic bricks. No details have been published, but an examination of the bricks suggests that the method used resembles closely one of those described above for stabilising the lime.

The valuable properties of dolomite bricks are partly due to the fact that the most fusible mixture of magnesia and lime melts at 2300° C., so that dolomite and magnesian limestone can contain a relatively large proportion of impurities without being too fusible to use. Hence, small proportions of silica (even up to 20 per cent.) have little practical effect on the refractoriness of dolomite. The serious effect of silica is that it tends to form $2CaO.SiO_2$, which disintegrates ("dusts") on cooling and so destroys the bricks.

The most durable of plain dolomite bricks contain 86 per cent. of dolomite, 6 per cent. of ferrous oxide (or alumina), and not more than 8 per cent. of silica. Apart from these, the best dolomite bricks are dolomite-chromite bricks (p. 492) and dolomite-alumina bricks. In both cases, the calcium

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[1] Lather and Pitt, "New Canadian Refractories and their Applications," *World Power Conference*, **B1**, 1936.

oxide combines with chromite or alumina, forming a compound which is not easily affected by water and which also has ample refractoriness.

Dolomite bricks can have a greater resistance to slag and to spalling than have magnesia bricks, because dicalcium silicate is more resistant than magnesium silicate to dust and slags containing lime and iron compounds, but it is necessary that the dicalcium silicate should be fused and form a film over the remaining particles. It is also desirable to have a stabilising agent such as ferrous oxide or chromic oxide present to the extent of 7–8 per cent.

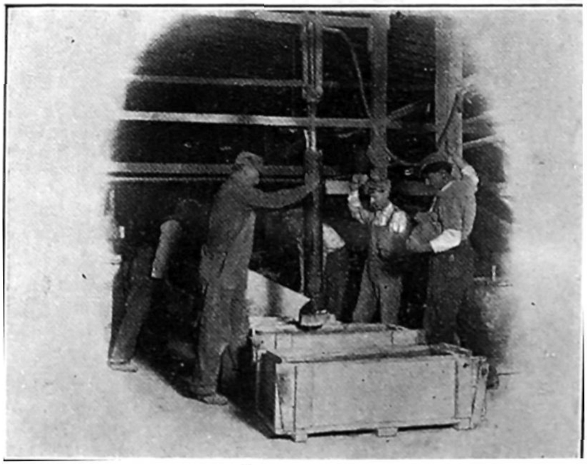
DOLOMITE-CHROMITE BRICKS.

Bricks made of dolomite and chromite have been used successfully. They are cheaper than magnesite-chromite bricks (p. 525) and less affected by water than most dolomite bricks. Their composition must be accurately adjusted so that all the impurities in the chromite are combined with lime or magnesia.

LIME BRICKS.

Lime is an extremely refractory substance which has never been fused by artificial means,[1] though clear yellow crystals of lime (CaO) may be found in the brickwork in the bottom of some steel furnaces.

Lime was one of the first substances used as a basic lining for steel furnaces (converters), its employment along with limestone and petroleum being included in E. Riley's (1878) and G. E. Dering's (1879) patents. In the latter, the bricks are formed in a press under " a pressure of 7 to 40 tons per square inch," and are afterwards burned " in the usual manner." Lime bricks have never been used extensively, as they are very difficult to produce, no really satisfactory bond for them having yet been found. A little silica is useless, and a large proportion produces too fusible a material. Bricks made



(Courtesy of Mr C. O. Grafton.)

FIG. 107.—Using a rammer driven by compressed air for making furnace linings.

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[1] Notwithstanding this, the manufacture of refractory articles of fused lime was patented in 1901 by C. G. Sudre and C. V. Thiery.

of crushed limestone bonded with a solution of silicate of soda, and dried, but not burned, were patented in 1877 by S. G. Thomas, and blocks cut direct from limestone and grouted in pitch or tar (as patented by H. Harmet in 1886) have proved fairly satisfactory for lining furnaces. Though cheaper, they are much inferior to magnesia bricks of good quality on account of the excessive shrinkage.

The extensive use of lime is now confined to ramming lime powder into those parts of the furnace where it is required.

The chief objection to lime as a refractory material is its low mechanical strength and the apparent impossibility of making it into durable bricks and blocks.

CEMENT BRICKS.

Bricks made of Portland cement are little more than a curiosity, though they possess characteristics of value for some purposes, such as the lining of rotary kilns in which cement is burned. The cement clinker is reduced to a coarse powder, and is mixed with sufficient finely ground cement and water to produce a mass which can be moulded into bricks or blocks in the same manner as concrete.[1] This process was patented by H. H. Lake in 1901, and the use of Portland cement with about 8 per cent. of starch by R. Middleton in 1903.

As Portland cement vitrifies and softens at temperatures below that usually regarded as the minimum in the definition of refractoriness given on p. 1, bricks made of it can scarcely be regarded as refractory, but their successful use in lining rotary kilns justifies their inclusion here.

BARYTA BRICKS.

So far as the author is aware, bricks made of baryta are not in regular use in any furnace, but their manufacture is the subject of two patents—one by J. B. Alzugaray in 1891, in which barium carbonate is bonded with limestone, magnesium carbonate, magnesia, alumina or silicate of soda, and the other by T. B. M'Ghie and E. G. Ballard in 1896, in which baryta is bonded with sodium sulphate.

The properties of baryta bricks should bear a close resemblance to those made of magnesia; they are understood to be specially useful in cupelling furnaces.

BASIC SLAG BRICKS.

Although basic slag is produced in a fused and fluid state in the manufacture of steel by the Thomas and Gilchrist basic process, the use of this material in the form of bricks and blocks has formed the subject of several patents, of which that of A. E. Tucker in 1885 is the most important. The slag is granulated by running it in a molten state into water and afterwards crushing it still finer if desired.

The bond may be lime, magnesia, or alkaline salts, or a temporary bond such as tar may be used. The general process of manufacture is the same as that for magnesia or dolomite bricks, but bricks made of basic slag must be burned at a lower temperature, *i.e.* one below the softening-point of the slag.

Basic slag bricks are obviously inferior to those of less fusible material, but as the slag is cheap, these bricks may be used for those parts of a furnace which are not hot enough to spoil them. The manufacture of slag bricks

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[1] See the author's *Bricks and Artificial Stones of Non-plastic Materials* (J. & A. Churchill) for more detailed information.

without burning them is a commercial process of considerable importance,[1] but such bricks usually shrink too much to be used as a refractory material.

ZIRCONIA BRICKS.

Zirconia is commonly regarded as a rare earth, but under favourable circumstances the price has several times been so low that bricks made of zirconia have proved cheaper than those made of magnesia, whilst possessing the great advantage of being far less sensitive to sudden changes in temperature.

Uses.—Bricks and other articles made of zirconia are basic in character and serve the same general purposes as those made of magnesia, though they are more refractory and less sensitive to sudden changes in temperature.

It is possible that zirconia may be very suitable for the roofs and linings of electric furnaces, but zirconia bricks have been disappointing in so many cases that it is not easy to recommend them. They are very resistant to silica and to glass, but not to basic slags or to abrasion. Zirconia bricks are highly refractory, and under many conditions appear to be inert; as greater progress is made in their manufacture zirconia may eventually prove to be one of the most valuable refractory materials.

Materials.—The chief constituent of these bricks is *crude oxide of zirconium*, but bricks of much superior quality and at a comparatively small increase of cost are produced from the purified zirconia, containing about 99 per cent. of the oxide; the use of mixtures of zirconia with sillimanite, alumina, silica, or chromite has also been patented. The zirconia should have been heated to at least 1400° C. (preferably 1800° C.) before use, so as to convert it into a non-shrinking form, as otherwise the bricks will shrink and warp excessively during manufacture and, possibly, in use. Thoria, magnesia, and zirconium hydroxide may be added to reduce the shrinkage without seriously affecting the refractoriness.

Fused zirconia is the best form, but it is so costly and so difficult to grind that its use for anything larger than small crucibles is scarcely practicable.

Bonds.—Many bonds have been tried, but most of them with poor results. *Phosphoric acid*, *water-glass*, and *lime* give poor results. *Silica* should on no account be used, as it lowers the melting-point of the zirconia and gives the ware a bad "ring" when struck. It also volatilises very rapidly, and makes the firing of the goods containing it very difficult. A concentrated solution of magnesium chloride is better, but the chlorine in it is objectionable. *Magnesia* is also unsuitable, as it volatilises even more rapidly than silica, and though it gives a pure white body, the latter is extremely porous and, consequently, the goods made from it are unsuitable for use with slags, etc. A German firm, however, have successfully used a mixture of 10 parts of magnesia and 90 parts of zirconia, together with phosphoric acid, the ware being burned at 1400° C. to 1500° C.

According to Cornstock [2] the dead-burned magnesite should be mixed with an equal weight of refined zircon sand, and the finely ground (100-mesh) mixture should be mixed with one and a half times its weight of zircon, moistened with lignin or other temporary bond and then made into clots which are burned at 1500° C. The product is ground to 100-mesh, mixed with twice its weight of coarse dead-burned magnesite and made into bricks.

The addition of 2 per cent. of dead-burned magnesia has been found by several investigators to reduce the cracking of zirconia bricks by preventing

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[1] See the author's *Bricks and Artificial Stones of Non-plastic Materials* (J. & A. Churchill) for more detailed information.

[2] *J. Amer. Cer. Soc.*, 1933, **16**, 29.

the inversion of monoclinic to tetragonal zirconia (p. 241). This is quite distinct from its use as a bond.

Alumina is more suitable, as it only lowers the melting-point to a very slight extent, and 3·5 per cent. of it may be added without any injurious effect to the properties of the zirconia.

Clay, to the extent of 3 to 5 per cent., gives a good strong body of a light ochre colour, but it generally makes the mixture too fusible for the purposes for which zirconia is used as a refractory material, though it may be used for zirconia bricks which will not be heated above 1700° C.

Ball clay has been used successfully without unduly reducing refractoriness. China clay has not sufficient binding power.

Chromic oxide (0·5 to 1·0 per cent.) has been used satisfactorily, but as it is non-plastic it is difficult to regard it as a bond.

Borax and *boric acid* appear to be unsuitable.

Sodium carbonate has too little binding power and too great an effect on the refractoriness.

Thoria is very satisfactory as a bond, and raises the melting-point of the mixture 10° C. to 30° C., whilst yttria is even more active, and, with 6 per cent., the melting-point of the mixture is raised to 43° higher than the melting-point of pure zirconia.

Organic materials have also been tried, but they have the disadvantage of leaving a very porous mass which is unsuitable for many purposes. The chief organic materials which have been used are: colophony, oil of turpentine, celluloid in amyl acetate, glycerin, and caramel, the last two being the most satisfactory.

Zirconia.—Although all the foregoing binders have been used with more or less success, the best binder of all is zirconia itself in the colloidal state, as in this case the ware may be entirely made of zirconia.

Colloidal zirconia is prepared by evaporating a solution of zirconium nitrate to dryness, dissolving it in water and repeating the process four times. This treatment produces a suspension containing about 2 per cent. of colloidal material, which must be freed from any injurious electrolytes before using as a bond.

Schwerin grinds the zirconia to a very fine state and then suspends it in water, the resultant slip being very satisfactory for mixing with the coarse zirconia for casting, as the colloidal zirconia particles readily remain in suspension and so enable the casting to be carried out very simply, no difficulty being experienced in withdrawing the ware from the moulds if the mixture has been properly prepared.

According to E. Podszus (Brit. Patents 11,771—1912; 3118—1913), it is merely necessary to add to the powdered zirconia a solution of zirconium nitrate or chloride and then to dialyse in order to remove the acid. In another method by the same inventor the material is made into a slip by grinding it to particles ·005 to ·0001 mm. diameter and mixing with a solution of gelatin or gum, or a salt of zirconium, such as the nitrate. This bond is mixed with the zirconia powder, not less than 0·5 per cent. of bond being used, but avoiding an excess (4 to 6 per cent. average). Satisfactory results have also been obtained by using a mixture of 10 parts of zirconia, 88 parts of dead-burned magnesia, and 2 parts of a solution of magnesium chloride of specific gravity 1·22.

Ryschkewitzsch has found that the most satisfactory mixture consists of highly calcined zirconia with 2 to 4 per cent. of zirconium carbonate ground together and then made slightly acid.

Grinding and Mixing.—The calcined zirconia is first ground to powder, care being taken not to have too much fine material present. Better results are obtained if the material is graded before using. Some zirconia is so hard that a ball-mill is essential.

If the hand-moulding process, the stiff-plastic or the dry-pressing process is employed, the calcined zirconia is treated with water—preferably immersed in it, for a week or more, as imperfectly wetted material has a low crushing strength when made into bricks, and cracks very easily when heated. A charge of about 5 cwts. of the material is then mixed, in a small edge-runner mill with a revolving pan, with a suitable quantity of the bond. The mill should be run for about 20 minutes. The mixed product, when squeezed in the hands, should not be sufficiently wet to adhere to the hands, nor should it be so dry as to crumble to pieces, or it will not be sufficiently strong when moulded.

Manufacture.—Four methods may be employed in the preparation of zirconia bricks—

(1) Hand-moulding.
(2) Stiff-plastic pressing.
(3) Dry-pressing.
(4) Casting.

In the *hand-moulding* process, the paste is thrown forcibly into a wooden mould, and then turned out on to a pallet board, after which it is dried slowly for several weeks, the moulding process being almost the same as for hand-made fireclay bricks. Owing to the skill involved in this process, it is often much quicker to use the stiff-plastic or dry-pressing process.

In the *stiff-plastic process*, it is necessary to use a paste which is rather stiffer than that used for hand-moulding. This is shaped in a press. For crucibles and other small articles a hand-driven screw press may be used, but for bricks a power-driven press (fig. 48) should be employed. The general process is the same as that described in Chapter II.

In *dry-pressing*, the particles of calcined zirconia should be suitably graded before mixing, as, in order to secure a strong dense body, it is essential that the particles should interlock as much as possible with each other so as to leave a minimum amount of space or interstices between them. A convenient quantity of the mixture of calcined zirconia and binder in the form of a damp powder is placed in the die of a press and subjected to a pressure of 4000 lbs. per square inch in the cold, or, if the mixture is heated, the pressure should be 7000 lbs. per square inch. Instead of a single compression, it is better to submit the mixture first to a preliminary pressure, and after releasing it to allow any trapped air to escape, to apply the final pressure. Unless this treatment is adopted, the air enclosed in the material will expand on heating, and may break the article. The presses shown in figs. 51 to 53 are suitable, and the general procedure is the same as that described in Chapter II.

In *casting*, the zirconia is ground with an equal weight of water and sufficient finely ground zirconia to act as a bond, so as to form a slip or slurry similar to that used in casting claywares (Chapter XII.). This slip is poured into plaster moulds, which are then allowed to rest until a sufficient amount of material has been deposited. The surplus liquid is then poured off and the mould set in a warm place to dry. The partly dry article is removed from the mould as soon as it is stiff enough to be handled. Casting the electrically fused zirconia by pouring it into moulds and cooling slowly was patented in 1926 (Eng. Pat. 265,847).

Drying.—Zirconia articles when made by the wet process and by casting require prolonged and very careful drying. Those made by the stiff-plastic process may be dried more readily, and those made by the dry process can be dried rapidly.

Burning.—The bricks should be burned at a temperature higher than that at which they will be used, unless the latter exceeds about 1750° C., when higher burning temperatures are wasteful. Bricks, etc., made of impure zirconia can be burned satisfactorily at a lower temperature than those of purer zirconia, but the impure materials will have a much lower " maximum safe temperature " when in use. The burning should be prolonged sufficiently to produce bricks with a good ring which do not shrink seriously on re-burning at the same or a rather higher temperature. A. L. Duval d'Adrian (U.S. Pat. 1,430,724) heats the articles to redness in any convenient manner and afterwards " completes " the firing by heating them electrically to above 2500° C.

Properties.—Zirconia bricks and other articles, when burned, shrink about 10 per cent. of their original volume, but the shrinkage varies with the size of the particles, and some specimens (composed chiefly of very finely powdered zirconia) have been found to shrink only 3 to 5 per cent. Much more satisfactory articles are produced if the zirconia has been heated to 1400° C., or above, before it is ground ready for use.

Zirconia bricks, when subjected to a load of 50 lbs. per square inch, lose their shape at 1450° C. to 1600° C. V. Bodin found that the crushing strength of crude zirconia decreases on heating to 800° C., then increases up to 1000° C., after which it decreases gradually to zero.

Zirconia bricks are chiefly characterised by their high refractoriness, low thermal conductivity, low coefficient of expansion, and great resistance to slags. Zirconia is particularly resistant to the action of slags, chemicals, and fumes, which are very destructive to most refractory materials at the highest temperatures encountered in furnaces. It is equally resistant to acid and basic open-hearth slags, fluorspar-lead slags, many metallic oxides, and to various molten chemicals such as borax, but iron sulphide, sodium carbonate, hydroxide and bisulphate, fluorspar and all fluor-bearing minerals, corrode it and eventually dissolve it when heated to a sufficiently high temperature.

The refractoriness of zirconia bricks is 2400° to 2600° C., unless a large proportion of bond has been used. The refractoriness under a load of 14 lbs. per square inch is 1600° to 1650° C. The crushing strength is double that of fireclay bricks, but zirconia bricks are very brittle.

Zirconia bricks are inert to most chemicals.

The *thermal expansion* of well burned zirconia bricks is 0·38 to 0·56 according to the temperature at which they have been burned. According to Cohn[1] zirconia which has only been heated for a short time at 900° to 1100° C. has a reversible expansion, but heating to a higher temperature makes it irreversible.

Pure zirconia is converted from a monoclinic to a tetragonal form at 1000° C., but the original form is restored on cooling slowly.

A compound corresponding to $Mg_2Zr_3O_8$ shows no permanent change below 1400° C.

The thermal conductivity[2] is 0·0036 g.-cal./cm./° C./sec. On account of its very low conductivity bricks made of zirconia may, when white hot, be plunged into cold water without risk of fracture.

The specific gravity of fully shrunk zirconia is 4·8 to 5·0.

The specific heat of zirconia at different temperatures, according to Wilson, Hildcroft, and Mellor, is as follows :—

600° C.	0·137
1000° C.	0·157
1200° C.	0·167
1400° C.	0·175

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[1] *Ker. Rund.*, 1930, **38**, Nos. 48–52.

[2] F. H. Norton, *J. Amer. Cer. Soc.*, 1927, **10**, 30–52.

The electrical resistivity of zirconia bricks, according to Hartmann, Sullivan, and Allen,[1] is as follows :—

TABLE LXXXI.—ELECTRICAL RESISTIVITY OF ZIRCONIA BRICKS.

Cold.	Less than 134,000,000 ohms per centimetre cube.
800° C.	„ 558,000 „ „ „
900° C.	„ 224,000 „ „ „
1000° C.	„ 131,000 „ „ „
1100° C.	„ 53,800 „ „ „
1200° C.	„ 7,710 „ „ „
1300° C.	„ 2,100 „ „ „
1400° C.	„ 968 „ „ „
1500° C.	„ 412 „ „ „

The chief disadvantage of zirconia articles is that, on heating, it tends to form the nitride and carbide, which are harmful.

For zirconia crucibles, scorifiers, etc., see Chapter XII.

ZIRCON BRICKS.

Zircon or zirconium silicate (p. 240) has been used for making bricks, but the natural mineral is so irregular in composition that the bricks are inferior to those made of purified zirconia. When made of carefully purified calcined zircon or of fused zircon the bricks are more resistant to slags than are silica bricks.

Rees and Chesters [2] and Cornstock [3] have made bricks of various proportions of magnesia and zircon. The former prefer a 50–50 mixture, but Cornstock states that bricks of a 20–80 mixture burned at 1480° C. are the best.

Bonds.—The most suitable bonds for zircon bricks are dextrin, tar oil, starch, flour, borax, potash, phosphates, clay, lime, and magnesia, or mixtures of these.

Properties.—The bricks are resistant to spalling and to basic slags, but not to acid slags.

The refractoriness is lower than that of zirconia bricks.

The specific gravity of zircon is 4·6; that of zircon-magnesia bricks about 3·5.

The coefficient of expansion of zircon-magnesia bricks is about the same as that of magnesia bricks; that of zircon is much less. The thermal conductivity is 0·0040 to 0·0073 g.-cal./cm./° C./sec. The porosity is about 26 per cent.

TITANIC OXIDE BRICKS.

The manufacture of bricks from crushed ilmenite or titanic iron ore together with lime and water was patented (Eng. Provis. Pat. 4275 (1878)) by Gjers, who suggested that the same mixture could also be employed for pugged or rammed linings for Bessemer converters.

The British Thomson-Houston Co. in 1912 patented the use of a mixture of 15 parts of silica, 12 parts of carbon, and 20 parts of rutile or titanium oxide as a refractory material.

E. Podszus has suggested the following bonds for articles made of titanic

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[1] *Trans. Amer. Electrochem. Soc.*, 1920, **38**, 279.

[2] *Trans. Cer. Soc.*, 1930, **29**, 309.

[3] *J. Amer. Cer. Soc.*, 1933, **16**, 28.

oxide: water, colophony, oil of turpentine, celluloid in amyl acetate, glycerin, and caramel, the last two being the most satisfactory.

The use of a mixture of chemically prepared titanium oxide with clay or various other substances was patented in 1934 (Eng. Pat. 445,495).

Bricks composed of magnesia and titanium oxide are refractory, but very costly. The magnesia-titanium oxide system[1] has three eutectic points:

(i) at 10 per cent. of magnesia, melting at 1650° C.;
(ii) at 30 per cent. of magnesia, melting at 1620° C.;
(iii) at 62 per cent. of magnesia, melting at 1800° C.

The chief objection to bricks made of titanic oxide is their great cost; otherwise they are valuable as refractory materials.

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[1] Wartenburg and Prophet, *Zts. anorg. u. allg. Chemie*, **208**, 375.

CHAPTER V.

BAUXITE AND OTHER HIGHLY ALUMINOUS BRICKS.

PURE alumina is one of the most refractory materials known, so that it is not surprising that it is used in various forms for the manufacture of refractory bricks. As alumina is entirely devoid of plasticity, the particles must be cemented together with a suitable bond.

Pure alumina is too costly for use as a brickmaking material, though bricks made of molten alumina have been made on a small scale by fusing alumina in an electric furnace until it becomes a thin fluid and then casting it in moulds made of fine sand or grog in a manner similar to casting metal. The loss by cracking during cooling is very heavy, and the cost of manufacture is too great to be profitable. The native ore (bauxite) is, therefore, the form in which alumina is generally used by brickmakers, though for some specially highly refractory articles a mixture of china clay and pure alumina, or fused alumina which has been ground or reunited with a suitable bond, is employed.

Alumina (or bauxite) is also used extensively to increase the refractoriness of fireclay bricks by mixing the clay and bauxite together. Bricks made of such a mixture are frequently known as bauxite bricks. Hence, there are two distinct kinds of aluminous or bauxite bricks—those composed of almost pure alumina with not more than 20 per cent. of bond, and those made of fireclay to which a considerable proportion of bauxite has been added. The latter would be more correctly described as *semi-bauxite bricks*. Bricks made of fused alumina are described in a later section.

Uses.—The use of bauxite bricks is largely confined to cases where a pure refractory material with a high proportion of alumina as well as a very high melting-point is needed. They are chiefly used where molten metals, metallic oxides, or basic slags are heated to very high temperatures, as in the manufacture of steel in Siemens and Martin furnaces, and for lining rotary cement kilns.

In furnaces in which the brickwork is particularly liable to be attacked by alkalies, bauxite bricks are preferable to fireclay or silica, but the bricks must be composed almost wholly of bauxite, and not of fireclay "improved" by the addition of bauxite.

Under the conditions which obtain in basic open-hearth steel furnaces at the Bethlehem Steel Works, the best bauxite bricks have been found to be more refractory and more impervious to slag than magnesia bricks, but notwithstanding this advantage they are not extensively used by steel manufacturers.

Bauxite bricks are also more refractory and durable than those made of magnesia in lead-refining furnaces. When well made, they are exceptionally resistant to corrosion.

Fused bauxite bricks (alundum bricks) have been used satisfactorily for the roofs of electric furnaces. They are sufficiently satisfactory as regards refractoriness, but are seriously corroded by the vapours arising from intensely heated slags.

Preparing the Materials.—As explained on pp. 204 to 207, the purer bauxites should alone be used,[1] and they should be carefully picked and then burned before being made into bricks.

Some bauxites may be made sufficiently pure by crushing the material to powder and then washing it in a vigorously agitated stream of water or in an ore-treating plant. The relatively lighter silica and the denser impurities may be largely separated by this means.

The burning may be effected by heating the lumps of bauxite in a shaft-kiln or even in a continuous or a down-draught kiln, but the following method is more common, as it enables the smaller pieces of bauxite to be used:—

The material is crushed in an edge-runner mill to a coarse powder and is mixed with one-tenth of its weight of plastic fireclay and sufficient water to form a plastic paste. The mixture is passed through a pug mill and is then made into rough bricks or clots either by hand-moulding or by the wire-cut process. The clots are then dried and burned at the highest temperature reached in a kiln otherwise filled with firebricks.

Washed bauxite cannot be burned in a vertical shaft, as it packs and obstructs the passage of the kiln gases, nor can it be burned in a down-draught kiln for the same reason. The only satisfactory method is to burn it in a rotary kiln, or to mix it with clay and make it into rough clots.

The temperature attained in this first burning should correspond to Seger Cone 13 (1380° C.) or above. It is useless to heat it below Cone 10 (1300° C.), as it is only above this temperature that the greater part of the shrinkage occurs. If a still higher temperature is reached, bauxite becomes almost as hard as emery, and is capable of great resistance to mechanical abrasion.

The burned bauxite is crushed to a coarse powder like grog, and is then ready for use.

Some bauxites possess the disadvantage of losing shape at temperatures below those at which they should be burned. This is not due to impurities present, but is probably caused by some unknown rearrangement of the molecules. If such bauxites are mixed with normal bauxites, the mixture is usually free from this objection.

The crushed, burned bauxite should be very carefully graded into particles of suitable sizes. Few brick manufacturers devote sufficient attention to this. The sizes of grog particles mentioned on p. 144 are usually suitable for bauxite, though some manufacturers maintain that granular bauxite softens when heated and will not stand superimposed weights and pressure, and they therefore prefer a finely powdered bauxite.

The following *bonds* may be used for uniting particles of bauxite:—

(*a*) *Clay*, usually fireclay, is a good bond. The greater the plasticity of the clay the better, provided that the clay is not too fusible, so as unduly to reduce the refractoriness of the mixture. The use of *bentonite* as a bond has been patented by Z. Olsson (U.S. Pat. 1,442,413).

(*b*) *Silica*.—J. Bach in 1904 patented the use of 12 parts of quartz to every 100 parts of bauxite. I. Werlein (Eng. Pat. 11,846, 1911) suggests the use of

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[1] Some users affirm that bauxite containing 20 per cent. of silica, but not more than two-thirds of the percentage of alumina present, makes stronger and more durable bricks than those made of purer bauxite. They consider that the silica acts as a bond.

a mixture of 80 to 95 per cent. of alumina, 5 to 20 per cent. of silica, and small quantities of titanic acid, beryllia, zirconia, or other natural minerals.

(c) *Lime*, usually as milk of lime (patented by W. J. A. Dundonald in 1885), is used in the same manner as for silica bricks.

(d) *Magnesia.*—A bond composed of magnesium chloride and lime was patented in 1886 by A. Fould and P. Genrean. Magnesia may also be used to form a bond consisting of artificial *spinel* or magnesium aluminate. The following mixture is recommended by A. A. de Karyscheff (Brit. Pat. 2994, 1907):—Alumina 102 parts, magnesite 40, agglutinant 16, boracic acid 3, naphtha residue 2, and water 5 parts. The agglutinant is made by heating "vegetable matter with aluminium and magnesium hydrates and an alkaline solution at 200° C. under a pressure of 12 to 15 atmospheres."

(e) *Plaster of Paris*, patented by F. Engelhorn in 1906.

(f) *Silicate of soda* (water-glass), patented by J. Burch and R. Allen in 1882. Bricks made with silicate of soda as a bond are less resistant than those having some other bond, but where there is little load to be supported, the silicate bond is very satisfactory, as the bricks dry at atmospheric temperature and are quite resistant up to 1400° C., and often to a much higher temperature.

(g) *Aluminium nitrate*, made slightly acid with nitric acid. This was patented by E. Podszus in 1912. It is supposed to form a colloidal solution, the particles of which enmesh in the coarser particles of bauxite and produce a plastic mixture.

(h) *Temporary bonds*, such as *tar*, heavy *mineral oils*, molten *paraffin wax*, etc.

Of these various bonds, the most important are (a) clay and (b) lime, the others being more of an experimental nature. Mineral bonds have so great an advantage over tar and other temporary bonds that the use of the latter for bauxite bricks is seldom desirable.

Lever, Holland, and Todd in 1890 patented the manufacture of bricks from alumina or aluminium hydrate by placing the powdered material in moulds, which are then heated to incandescence for three hours, or until the alumina becomes hard. The moulds are necessary in order that the material may retain its shape. The patentees claim that bricks so made will not disintegrate with sudden changes of temperature, particularly on alternate heating and cooling.

Manufacture.—There are four important methods of making bauxite bricks—[1]

(a) *Bauxite bricks made without a bond.* These must be made by the semi-dry method. They are usually so weak as to be almost useless. When no bonds can be used, it is customary to tamp the bauxite into position in the furnace rather than to make bricks of it.

(b) *Bauxite bricks with a clay bond* are made by mixing the burned, crushed, and graded bauxite with about one-tenth of its weight of binding clay, and with sufficient water to make a lean paste. This mixing may be effected in a trough mixer, or in an edge-runner mill. Sometimes the clay and bauxite are mixed in a dry state, the water being added afterwards and the materials being then re-mixed in a trough mixer.

It is essential that the proportion of clay should be as small as possible, as the clay is less refractory than the bauxite, and will, therefore, lower the heat resistance of the latter. The only means of keeping the proportion of clay within reasonable limits is to use a highly plastic binding clay; the common plan of using fireclay has the serious disadvantage of employing a

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[1] When any of the less important bonds just mentioned are used, the method of manufacture of the bricks usually corresponds to one of those described in the text.

lean clay, of which a large proportion is necessary to secure the bonding effect desired. For this reason, many bauxite bricks contain 25 per cent. or more of added clay; indeed, P. Mersch in 1898 patented the use of 8 parts of fireclay, 6 of bauxite, and 1 of china clay. Such bricks closely resemble *semi-bauxite* bricks (see (*d*) below).

The mixture may be made into bricks by hand-moulding, by the wire-cut process, by the stiff-plastic process, or by the semi-dry process. Of these methods, hand-moulding is the most generally adopted, and, so far, appears to be the most satisfactory. The use of the semi-dry process for bauxite bricks is, however, deserving of more attention than has yet been paid to it.

(*c*) *Bauxite bricks with a lime bond* are produced in a precisely similar manner to silica bricks. The burned and crushed bauxite is mixed with sufficient lime-water or milk of lime to produce about 3 per cent. of lime in the finished bricks.

The use of lime as a bond has been found to be quite satisfactory; the lime appears to combine with the silica which occurs as an impurity in all bauxites, forming a hard silicate bond. If the percentage of lime does not exceed about 2 per cent., the refractoriness of the bauxite will not be seriously diminished.

As a mixture of clay and lime or too much lime would seriously reduce the value of the bricks, it is important that the crushed, burned bauxite should have been made from as pure a bauxite as possible.

(*d*) *Semi-bauxite bricks* consist of a mixture of fireclay and bauxite in almost equal parts, or of a mixture in which the fireclay preponderates. They bear a close resemblance to firebricks to which a little grog has been added, or in which the grog has been replaced by burned bauxite, and are made in a similar manner (see Chapter II.).

The addition of bauxite to fireclay increases the percentage of alumina in the clay, reduces the shrinkage similarly to grog, and simultaneously raises the refractoriness of the clay. On the other hand, this use of bauxite generally makes the mechanical strength of the bricks somewhat less than when fireclay grog is used.

Bauxite is considered by some metallurgists to be unsatisfactory as an addition to clay, but the extensive use of mixtures of fireclay and bauxite under the most trying conditions of furnace work shows that if the mixture is properly treated, satisfactory bricks can be produced. It is important to observe, however, that the addition of bauxite does not make a poor fireclay into a good one, and that a mixture of clay and bauxite with the same proportions of alumina, silica, and fluxes as a high-grade fireclay will not behave like the latter, for in the mixture the whole of the alumina is not combined with the silica, as in a true clay. Hence, the addition of bauxite to clay is a matter requiring considerable thought, and the indiscriminate manner in which it is recommended by some writers cannot be too strongly deprecated. In any case, the bauxite must be burned before use, or it will cause damage by excessive shrinkage.

Drying.—Bricks are dried on a steam- or fire-heated floor or in tunnels.

Burning.—Unburned bauxite bricks will not stand much pressure, and must not be stacked in high courses. Usually, they are burned on the top of other goods. The bricks must be protected from "flashing" and flame, and plenty of air must be admitted to the kiln; otherwise, any iron oxide in the bauxite will be reduced and spoil the bricks.

The kiln may be of any of the types suitable for firebricks, but the number of bauxite bricks made at a time being limited, they are usually burned in single down-draught kilns along with silica or fireclay bricks.

The burning of bauxite bricks presents no special difficulties, except that a very high temperature—not less than 1250° C. (Cone 8) and preferably between 1400° C. and 1500° C. (Cones 14 to 18)—is desirable, though difficult to secure in a coal-fired kiln without reducing the iron oxide in the bauxite. Gas-fired kilns largely avoid this difficulty.

The **cooling** and **storage** should be under the same conditions as for fireclay bricks.

The two greatest difficulties experienced in the manufacture of bauxite bricks from good materials are—

(*a*) Weak bricks due to too little bond or imperfect mixing.

(*b*) Bricks which shrink in use, owing to insufficient heating in the kilns.

Both of these are "difficulties of manufacture," and can only be avoided by skilled oversight.

Properties.—The chief properties of bauxite bricks are the same as those of firebricks generally, but the distinguishing features are a high percentage of alumina and great refractoriness.

Shrinkage.—The chief drawback of bricks containing a large proportion of bauxite is their continual shrinkage when in use at high temperatures. Even when bauxite bricks have been burned at the highest temperature attainable in a kiln, they still continue to shrink when in use, and it has hitherto been found almost impossible to produce bauxite bricks of perfectly constant volume. If the temperature at which the bricks were burned during manufacture is below that corresponding to Seger Cone 10, the shrinkage of the bricks in use may be serious; with a higher burning temperature the shrinkage in use will be less, but it will still be noticeable. Finer particles of bauxite are more constant in volume on repeated heating than are the coarser ones.

The shrinkage of bauxite can be reduced by the addition of quartz, but this lowers the refractoriness of the bauxite and so produces bricks which are little, if any, better than those made of fireclay. Hence, the addition of silica to bauxite is not to be recommended.

The shrinkage can also be eliminated by making the bricks of *fused* bauxite (see p. 509).

The *changes in volume* are generally similar to those of fireclay bricks, but those due to silica are less noticeable. When in use the shrinkage continues as the temperature rises above that at which the bricks were fired, so that a high firing temperature is essential.[1]

Cracking is by no means uncommon among bauxite bricks, and is usually a result of the bauxite not having been burned sufficiently before use.

Composition.—The composition of bauxite bricks depends on the nature and amount of the bond used. It may be calculated approximately from the composition of the bauxite and the bond, neglecting the "Loss on Ignition" in each case.

Chemical Reaction.—Bauxite bricks are commonly regarded as basic, though in many ways they partake of a neutral character. Their alleged basic character is chiefly due to the fact that they are scarcely attacked by basic slags. The majority of alumina bricks are seriously affected by lime, though if the surface of the bricks is sufficiently compact they may be heated in contact with lime or slag for a long time without marked corrosion.

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[1] For further information on the thermal expansion of alumina bricks see Rigby and Green, *Trans. Cer. Soc.*, 1938, **37**, 375.

When finely ground mixtures of alumina and lime are heated together the melting-point of the mixture is much lower than that of either the lime or alumina separately, as shown in Table LXXXII.

Resistance to Slags.—Bauxite bricks are less affected by strongly basic slag than are the best fireclay bricks, and, though they are attacked by it to some extent a vitrified skin is soon formed, which prevents the interior of the brick from wasting away. This resistance to slags is partly due to the inertness of calcined alumina and partly to the very viscous nature of slags rich in alumina. Even a small proportion of alumina greatly increases the viscosity of the slag, which dissolves it and so reduces the rate of further solution.

TABLE LXXXII.—EFFECT OF HEAT ON MIXTURES OF LIME AND ALUMINA.

Molecular Composition.	Mols. Al_2O_3 to 1CaO.	Per Cent. CaO.	Per Cent. Al_2O_3.	Fusing-Point (Seger Cones).	
				Boudouard.	Neumann.
$12CaO+1Al_2O_3$	0·08	86·8	13·2	16	..
$6CaO+1Al_2O_3$	0·17	76·7	23·2	15	..
$4CaO+1Al_2O_3$	0·25	68·8	31·2	16–17	29
$3CaO+1Al_2O_3$	0·33	62·2	37·8	15	19–20
$2CaO+1Al_2O_3$	0·50	52·4	47·6	13–14	..
$1CaO+1Al_2O_3$	1·00	35·5	64·5	20–26	26
$1CaO+2Al_2O_3$	2·00	21·5	78·5	36	..
$5CaO+3Al_2O_3$	0·60	47·8	52·2	..	13–14
$3CaO+2Al_2O_3$	0·66	45·2	54·8	13	13
$6CaO+5Al_2O_3$	0·83	39·7	60·3	15	20
$3CaO+4Al_2O_3$	1·33	29·2	70·8	26	28
$3CaO+5Al_2O_3$	1·66	24·8	75·2	31	32
Al_2O_3	..	..	100	..	42

Refractoriness.—The heat-resistance of alumina bricks should correspond to Seger Cones 36 to 39. It is usually found that the purer the bauxite (*i.e.* the larger the percentage of alumina present) the greater will be the refractoriness of the bricks, but their mechanical strength will not be so great as that of those containing 20 per cent. or more of silica.

Refractoriness-under-load.—Bauxite bricks of good quality when heated under a pressure of 50 lbs. per square inch should not yield below 1500° C.

The *maximum safe working temperature* of bricks rich in alumina is not much (if any) higher than that of mullite bricks (1700° to 1750° C.), because, whilst any excess of alumina is in the free state, it cannot offset the fusibility due to the fusion of the mullite with any impurities present. Consequently, whilst the safe working temperature of alumina bricks increases with the percentage of alumina up to about 72 per cent. (*i.e.* to that in mullite), any higher percentage is of little value in this respect.

Spalling.—Some bauxite bricks spall badly—chiefly because the material has not been sufficiently heated before being made into bricks. Some spalling appears to be inevitable with bauxite bricks, as it is related directly to their alumina-content; the coefficient of expansion increases with the proportion of alumina present. Mullite and allied bricks composed of alumina and silica are free from this defect.

Mechanical Strength.—The bricks which combine mechanical strength with refractoriness to the best advantage are those made of a fairly pure bauxite with sufficient clay to produce a moderately plastic material. Clay-bonded bricks, containing less than 25 per cent. of a refractory clay, do not usually soften, under a load of 40 lbs. per square inch, below Cone 33 (1730° C.), and, under a pressure of 50 lbs. per square inch, they begin to lose their shape at 1350° C. to 1500° C. Large quantities of lime-bonded bauxite bricks have been made with a crushing strength of 10,000 lbs. per square inch. According to V. Bodin, bauxite bricks decrease in crushing strength on heating to 800° C., and increase again up to 1000° C., after which the strength decreases progressively. Corundum bricks act in a similar manner (see fig. 108).

Resistance to Abrasion.—This depends on the temperature at which bauxite has been burned. Under favourable conditions of manufacture, bauxite bricks are among the most resistant to abrasion. To ensure this the bauxite must have been adequately heated before being made into bricks, the proportion of clay present should not exceed 15 per cent. of the material (10 per cent. is much better), and the bricks should be burned at 1600° C.

Resistance to Slags.—This is not so high as is commonly supposed, as bauxite bricks are usually sufficiently porous for slags to penetrate readily. In lead-smelting furnaces, bauxite bricks are corroded more quickly than common fireclay bricks. The resistance is greatly increased if the bricks are made of alumina and silica (see " Mullite Bricks," p. 389).

The *electrical resistivity* of bauxite bricks, according to Hartmann, Sullivan, and Allen,[1] is as follows :—

TABLE LXXXIII.—THE ELECTRICAL RESISTIVITY OF BAUXITE BRICKS.

Cold.	Less than 133,000,000 ohms per centimetre cube.
800° C.	,, 109,000 ,, ,, ,,
900° C.	,, 32,500 ,, ,, ,,
1000° C.	,, 17,200 ,, ,, ,,
1100° C.	,, 9,200 ,, ,, ,,
1200° C.	,, 6,100 ,, ,, ,,
1300° C.	,, 5,600 ,, ,, ,,
1400° C.	,, 2,200 ,, ,, ,,
1500° C.	,, 1,100 ,, ,, ,,

Porosity.—A most important defect in bauxite bricks is a high porosity, which renders them less durable in actual service (especially in the presence of corrosive abrasive materials) than their other properties would indicate. This objection may be overcome by the use of fused bauxite, which is, however, much more expensive.

HIGH-ALUMINA BRICKS.

The term *high-alumina bricks* is used broadly for those containing more than 47 per cent. of alumina, *i.e.* a larger proportion than is contained in a calcined china clay (46·2 per cent.) or any burned fireclay when used alone. Between this and bricks made of almost pure alumina a very wide range of properties is possible, and the use of the term " high-alumina bricks " needs to be watched. The durability of such bricks is not always proportional to the alumina present, and some high-alumina bricks are no more refractory than some fireclay bricks.

As the purer grades of china clay and kaolin have a refractoriness equal to

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[1] *Trans. Amer. Electrochem. Soc.*, 1920, **38**, 279.

Seger Cone 34 (1750° C.), the high-alumina refractory bricks should have a refractoriness between this and Seger Cone 42 (2000° C.), which is the refractoriness of pure alumina.

DIASPORE BRICKS.

Diaspore is a hydrate of alumina, $Al_2O_3.H_2O$ (p. 202), with properties similar to bauxite, which is found in large quantities in Missouri, U.S.A. It should be calcined at 1200° to 1300° C. before use to eliminate the combined water and to increase the density of the material, but some brick manufacturers use a mixture of raw and calcined diaspore. The calcining period may be reduced if 2 per cent. of finely ground tricalcium phosphate is added to the ground diaspore and the heating is effected at 1500° C. The calcined diaspore has so little plasticity that it is usually necessary to add 10 to 20 per cent. of refractory clay (fireclay, kaolin, or ball clay) to act as a binder (see U.S.A. Pat. 1,491,567—1924).

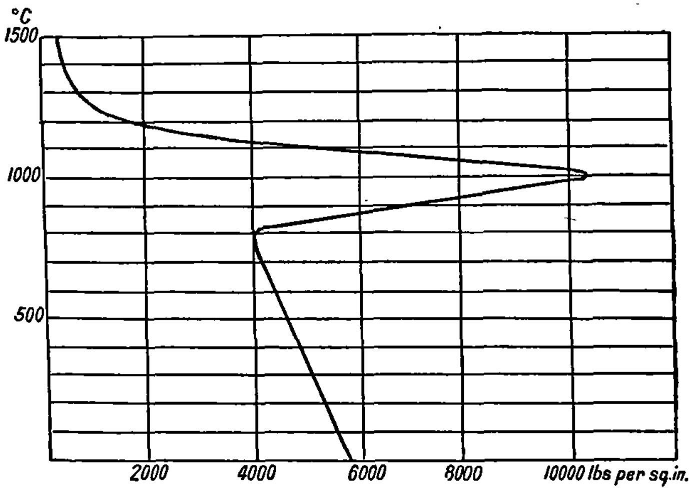

FIG. 108.—Strength of white bauxite (V. Bodin).

The bricks are made in the same manner as bauxite bricks (p. 502) and should be burned at 1400° C. or above. They are usually made of a mixture of 55 parts of calcined diaspore, 35 of raw diaspore and 10 of binding clay. They contain about 70 per cent. of alumina. Similar bricks containing only 60 per cent. of alumina have also been proved to give satisfactory results.

Their properties closely resemble those of bauxite bricks (p. 504), but some diaspore bricks have a longer range of vitrification.

Bricks made by fusing a mixture of diaspores are sometimes known as *Corhart bricks* (p. 512).

The American Society for Testing Materials has proposed the following definitions (C71 to 37T):—

50 per cent. Alumina-Diaspore Refractories.—Those having diaspore or nodular fireclay as an essential original constituent, and alumina-content of 50 ± 2·5 per cent. and a refractoriness not less than Cone 34.

60 per cent. Alumina-Diaspore Refractories.—Similar to the 50 per cent. material, but with 60 ± 2·5 per cent. of alumina and a refractoriness not less than Cone 35.

70 per cent. Alumina-Diaspore Refractories.—Similar to the 50 per cent. material, but having an alumina-content of 70 ± 2·5 per cent. and a refractoriness of not less than Cone 36.

SAND-BAUXITE BRICKS.

Bricks of apparently good quality have been made in this country from mixtures of sand and bauxite, united by a plastic clay. The objection to such a mixture is the incompatibility of its constituents; the clay shrinks on heating, whilst the sand expands and the bauxite (if properly calcined) remains unchanged. Three entirely different series of internal strains are thus produced, the result of which is to weaken the bricks; what frequently happens is that the clay cracks and becomes detached from the non-plastic grains, and the latter are moved out of place by the stresses to which they are subject. To avoid such difficulties, it is necessary to abandon the use of both sand and bauxite together with clay, and to use clay with either sand or bauxite, but not with both.

SPINEL BRICKS.

Spinel bricks are made by mixing equal parts of magnesite and white bauxite together, calcining them at a temperature not less than 1300° C., grinding the product and making it into bricks with the aid of a little ball clay. The final product should contain, as nearly as possible, 28·17 per cent. of magnesia and 71·83 per cent. of alumina, and so correspond to the formula of true spinel, $MgO.Al_2O_3$ (p. 235). It is essential that the magnesia and alumina shall be chemically combined, and for this reason electrically fused spinel is superior to that prepared in a blast-furnace or kiln. See U.S.A. Pat. 1,373,854 (1918); Eng. Pats. 302,087 (1928); 324,312 (1928); also patents for chrome spinels (p. 529).

Instead of using prepared spinel and a bond, the molten spinel may be poured into moulds (Eng. Pats. 391,662 (1931), 418,859 (1933), and the patents mentioned above). Other spinel mixtures are described on p. 718.

The refractoriness of spinel bricks depends on the purity of the aggregate and the proportion of ball clay used as a bond. The best bricks have a refractoriness of about 1950° C. The refractoriness-under-load is about 100° below the normal refractoriness unless an excess of bond has been used. The resistance to slags, metals, and reducing agents is exceptionally high. The resistance to abrasion is satisfactory. Spinel bricks have a very low thermal conductivity and are highly resistant to reducing conditions. They are liable to spall badly. Chrome-spinel bricks appear to be more resistant to sudden changes in temperature than are bricks made of magnesia-spinel.

When spinel bricks rich in silica are heated to about 1500° C. cordierite ($2MgO.2Al_2O_3.5SiO_2$)[1] is formed, with a low coefficient of thermal expansion and a refractoriness of about 1400° C. This material has a very short range of vitrification.

Strassen[2] has found that if an oxide is in contact with a spinel with which it does not form a solid solution, the spinel will tend to be decomposed. Thus lime tends to convert magnesium aluminate into calcium aluminate, which is much less refractory.

In short, spinel bricks have similar properties to magnesia bricks, but a rather higher refractoriness-under-load, lower expansion and rather higher thermal conductivity than silica and fireclay bricks. The tendency to spalling

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[1] Krause and Jakel, *Ber. deut. ker. Ges.*, 1934, **15**, 498.

[2] *Tonind. Ztg.*, 1934, **58**, 1146.

appears to vary greatly in bricks from different sources; in some bricks it is very great.

Spinel bricks are particularly suitable for metallurgical furnaces, as they are highly refractory and resistant to corrosion.

Chrome-spinel bricks are described on p. 529.

BRICKS MADE OF SINTERED BAUXITE.

Sinter-corund was first made in 1927 by Gerdien and Reichmann in the Siemens and Halske A.G. research laboratory. It is an almost pure alumina which has been heated sufficiently to sinter the particles without complete fusion. Bricks made of this material with clay or other suitable bond have a hardness of 9 on Mohs' scale, a specific gravity of 3·6 (as compared with 2·7 in those made of calcined alumina), a specific heat of 0·2796 at 0° to 1500° C. and a refractoriness approaching 1900° C. (sinter-corund melts at 2050° C.). Their thermal expansion between 20° and 800° C. is 80×10^{-7}, *i.e.* similar to steatite and double that of mullite and Berlin porcelain. The refractoriness under a load of 50 lbs. per square inch is such that no appreciable softening occurs below 1700° C. The electrical resistivity is high; at 300° C. it is 10^{13} ohm-cm., and at 800° C. 10^{8} ohm-cm. There is no after-expansion. The material is inert to nearly all chemicals and highly resistant to slags. (See also Eng. Pats. 382,071 and 410,988.)

BRICKS MADE OF FUSED ALUMINA.

For electric and other furnaces in which exceptionally high temperatures are reached, bricks or blocks made of fused alumina [1] may be used. They are of two kinds:

(i) Bricks made by using fused alumina as an aggregate, with clay or other material as a bond. Bricks of this class are often known as *coraffin, corundum, alundum,* or *corindite* bricks from the (trade-) names of the fused alumina used. Bergeron [2] has made bricks with great resistance to corrosion by bonding electro-cast grog with clay.

(ii) Bricks made by pouring the molten alumina directly into moulds and cooling the resulting "bricks" very slowly. These bricks are generally known by the trade name of *Corhart bricks* (p. 512), though this term should only be applied to bricks made by one firm.

The very great advantage of *coraffin, corundum, alundum, corindite,* and other bricks over those made of unfused alumina is the absence of shrinkage, combined with high resistance to abrasion and slags. If the alumina has not only been fused but has also crystallised, an almost ideal material is obtained. The importance of a crystalline structure is obvious, and in A. Bouvier's patent (1905) special directions are given to keep the crystals "as large as possible, so as to form a skeleton which resists sudden cooling and shocks." The formation of large crystals is facilitated by surrounding the crucible or hearth of the electric furnace with a vacuum-jacketed vessel such as that patented by G. Pettigrew and E. Gerbel-Strover in 1911.

Amorphous alumina may be fused with an alkali such as soda, only about 5 per cent. of the latter being needed to convert all the alumina into the β-form (Eng. Pat. 454,599—1934).

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[1] The use of fused alumina for refractory articles was patented by C. G. Sudre and C. V. Thiery in 1901.

[2] *J. Soc. Glass Tech.*, 1937, **20**, 586T.

According to Eng. Pat. 294,179 (1927) the formation of crystalline alumina is facilitated by adding 0·5 to 2 per cent. of a fluoride or fluosilicate to the raw bauxite, calcining and using the calcined mixture for making bricks.

The fused or crystalline alumina is purchased in powder or grains, of suitable size, the material being usually sufficiently refractory without further treatment. If necessary, it may be partially purified by heating it with hydrofluoric acid and then washing thoroughly. This drastic treatment removes the impurities from the outside of the grains and roughens their surface in such a manner as to make the bond adhere better than to the untreated material. Potassium bisulphate is superior to hydrofluoric acid, but is more costly to use.

Some fused or crystalline alumina contains only 90 per cent. of alumina, but for bricks of the most refractory quality the almost pure (98 to 99 per cent.) alumina should be used. Care should also be taken not to mistake a name; for instance, *alumidon* contains about 20 per cent. of silica and only 70 per cent. of alumina. It can be made into bricks which are excellent for some purposes, but is not a pure alumina.

When alumina is heated in an electric furnace under reducing conditions, some *aluminium carbide* is formed. This is objectionable, as it is so readily decomposed by water. If air is present at the same time as the reducing conditions, *aluminium nitride* is formed by the abstraction of nitrogen from the air. The use of this nitride as a material for furnace linings has been patented by O. Serpek in 1910 and by the Société Générale des Nitrures in 1912. The claim is made that aluminium nitride is specially suitable for electric furnaces on account of its low conductivity at very high temperatures.

Bonded Bricks.—In bricks made with fused or crystalline alumina and a bond, the alumina should be free from dust, and it is better for it to contain no particles which would pass through a 100-mesh sieve.

Bonds.—The bonds used are chiefly *fireclay*, *plastic china clay*, and *ball clay*, but *silicate of soda* is sometimes used. The particles of alumina may also be united by *bauxitic clay* (patented by F. Quester in 1901), *cement* or *plaster of Paris* (patented by F. Engelhorn in 1906). Schwerin, in 1911, patented the use of a solution of acetic acid in water as a bond for corundum. According to Bigot, it is important to avoid the use of such bases as lime, magnesia, calcined dolomite, etc., in the manufacture of bricks of fused alumina, as they lower the refractoriness of the material. It is desirable to use two sizes of grains—coarse and fine—in the proportion of 7 : 1 or thereabouts, and to add the bond in a finely divided state. Boehme und Söhne, in 1902, patented the use of 64 parts of granulated corundum, 9 parts of fine corundum powder, and 27 parts of plastic clay (preferably the highly plastic Klingenberg clay). The bricks are moulded and then burned in the same manner as bauxite bricks. A bond for use with crystalline alumina, consisting of a mixture of clay, flint, whiting, and magnesia, and maturing at 1250° to 1300° C., was patented in 1930 (Eng. Pat. 361,167).

The use of fused alumina bonded with calcium, titanium oxide or with a mixture of magnesia and calcium fluoride was patented in 1930 (Eng. Pat. 326,279).

The use of a binder composed of substances successively soluble in each other when heated, so that it has a vitrification range of 300° C. somewhere between 1150° and 1900° C. was patented in 1928. Suggested binders are mixtures of alumina and felspar, of magnesia and calcium fluoride, and of diopside and forsterite (Eng. Pat. 326,560).

In 1907, the British Thomson-Houston Co. patented the manufacture of *alundum bricks*, using fireclay as a bond, with or without graphite, and burning the bricks at 1100° C. to 1300° C.

J. Windholz, in 1904, patented the use of a mixture of corundum and boron carbide, whilst the Norton Co., in 1917, patented the use of a fused mixture of bauxite and zirconia, together with small quantities of silica and iron oxides.

F. Engelhorn, in 1906 and 1907, patented a process in which alumina is mixed with one-quarter to one-tenth of its weight of boric acid, chrome oxide, iron oxide, magnesium oxide, zinc oxide, silica or other oxide, and the mixture is heated to fusion. The mass is ground to a coarse powder, made into bricks by means of a temporary bond such as *dextrin*, *tar*, or *paraffin*, and then burned. According to the patentee, the addition of magnesia and zinc oxide produces compounds very resistant to alkalies; the addition of chromium oxide and magnesia increases the resistance of the bricks to lime, cement, and glass.

An " interlocking crystalline bond " composed of a titanium compound, lime and titania or lime and a silicate was patented in 1930 (Eng. Pat. 326,279). This is claimed as a means of imparting high resistance to spalling. A similar product made by fusing alumina, silica, and lime is the subject of Eng. Pat. 409,315—1931.

Heavy metallic soaps and other organic salts of aluminium may be used as a bond (Eng. Pat. 367,828—1930).

The addition of hydrochloric or other mineral acid to alumina to make it plastic was patented in 1931 (Eng. Pat. 382,071; also 391,703, 396,234, 405,978, and 410,988).

The *chief weakness* of bricks made of fused alumina and a bond lies in the bond itself, which is, of necessity, less refractory than the aggregate.

Shaping.—The bricks are shaped (i) by hand-moulding, (ii) in presses, or (iii) by slip-casting. The last is the subject of Eng. Pat. 405,978.

Bricks made of fused bauxite should be burned at a temperature at least as high as that to which they are to be heated in use.

According to Bigot, alumina which has been fused and cooled does not shrink when below 1400° C., and up to 1850° C. the shrinkage is only about 3 per cent. The porosity of bricks made of the material is about 9 to 12 per cent. They are extremely resistant to abrasion, being about three times as durable as magnesia bricks and twice as durable as bricks of unfused bauxite. The resistance of bricks made of fused bauxite to corrosion is about the same as that of ordinary calcined bauxite.

Firebricks made of fused alumina, according to Hecht, have, when cold, a crushing strength of 675 tons per square foot; they show no deformation under a load of 50 lbs. per square inch at 1350° C., and some have recently stood for 22 heats in the roof of an electric steel furnace.

Bricks of Molten Alumina are made by fusing the material in an electric furnace, pouring the fluid into iron or sand moulds and cooling slowly; special care is needed in annealing (Eng. Pat. 265,847—1926). Instead of pure alumina (which is liable to disintegrate when used in glass-melting furnaces), it is found to be more practicable to use a mixture of alumina and clay in carefully controlled proportions (Eng. Pat. 265,847—1926). This forms a glassy bond of great strength, which fills the pores.

The use of a mixture of alumina with 2 to 10 per cent. of magnesia was patented in 1933 (Eng. Pat. 449,018). The magnesia combines with some of the alumina to form spinel (p. 235), which forms interlocking crystals of great binding power (see also Eng. Pats. 16,714—1906; 340,958, 409,315, and 422,474).

A mixture of alumina (60), clay (35), and lithia (5) fused in an electric furnace was patented in 1928 (Eng. Pat. 322,361).

A mixture of crystals of corundum and mullite in the proportion of 2 : 1, made by melting alumina with about 8 per cent. of silica, casting the molten mass and cooling rapidly to 1200° C. and then more slowly, was patented in 1934 (Eng. Pat. 454,947).

Other patents relating to fused alumina, with other substances, shaped by casting, include Eng. Pats. 454,946 and 455,236, and U.S.A. Pats. 929,517 and 1,944,616. (See also " Spinels " and " Spinel Bricks.")

For Corhart bricks and blocks made in the United States under Fulcher's patent (U.S.A. Pat. 1,615,750—1925 *et seq.*), diaspore from various sources containing 9 to 18 per cent. of silica is employed, and, when necessary, kaolin added to adjust the alumina-silica content to alumina 75 per cent., silica 20 per cent., the impurities making up the remaining 5 per cent.[1] The three-phase electric furnaces used for fusing the mixture are of the dipping electrode type with graphite electrodes, the temperature of the molten material being 1900° to 2200° C. Every two hours the furnace is tapped, and the molten material is run into moulds made of sand bonded with linseed oil and baked at 200° to 240° C. for a couple of hours. They are contained in an iron frame and are surrounded by further beds of sand to minimise damage by leakage.

The cooling must be very slow—sometimes 7 to 15 days or more—and to ensure this, a few hours after casting the articles are sometimes removed from the sand and surrounded by kieselguhr. Several methods of annealing are mentioned in Eng. Pat. 265,847 and in U.S.A. Pat. 1,615,750. The castings are cleaned and the insulating material is reclaimed. A considerable amount of waste material is produced, which cannot be remelted.

The blocks and bricks approximate to the composition of mullite (72 per cent. Al_2O_3 and 28 per cent. silica), but they usually contain 20–25 per cent. of α-corundum and a siliceous interstitial glass; some electro-cast bricks contain only 47 per cent. of mullite[2] and 40 per cent. of free alumina. The mullite so formed is different from that obtained by heating clays.

The electro-casting method has been greatly extended in recent years to mixtures containing chromic oxide, magnesia and alumina (see " Siemensite ").

Bricks of the Corhart type have a refractoriness equal to Seger Cones 37 to 38 (1820° to 1850° C.), with a very short vitrification range. They are vitreous and non-porous (less than 1 per cent.), with a linear coefficient of expansion of about half that of a fireclay brick. The bricks are too hard to be cut or worked, but can be ground on alundum wheels; however, this is so costly that it must be kept at a minimum. The hardness is 8; the volume-weight is 187 to 194 lbs. per cubic foot; the true specific gravity is 3·6 to 3·7; and the thermal conductivity 0·000006 between 15° and 900° C. and 0·0105 g.-cals./cm./° C./sec. between 0° and 1400° C.

The specific heat between 900° C. and 1700° C. is 0·27. The linear thermal expansion from 15° to 400° C. is $1{\cdot}37\times10^{-6}$, from 400° to 700° C. $3{\cdot}67\times10^{-6}$ and from 700° to 1350° C. $5{\cdot}58\times10^{-6}$. The refractoriness-under-load (2 kg. per square centimetre) is about 1800° C.

The cold crushing strength is said to be 28,446 lbs. per square inch, or 1820 tons per square foot.

The bricks are exceptionally resistant to slags, ashes and glass (see also p. 208).

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[1] According to U.S. Pat. 2,044,817 (1937) it is necessary to have 0·85 to 1·42 per cent. of alkali present to prevent cracking during the cooling.

[2] Partridge and Lart, *J. Soc. Glass Tech.*, 1936, **20**, 203.

Many refractory bricks are either low in porosity or highly refractory, but few have both these important properties simultaneously; this combination is one of the reasons for the success of Corhart and similar bricks.

Bricks very similar in many respects to Corhart bricks are *Monofrax bricks and blocks*, which are electro-cast in a similar manner to Corhart products. They were developed jointly by the Mellon Institute and the Carborundum Co., and fall into three general groups: (i) "*Monofrax* L," containing 90 per cent. or more of alumina and with a high α-alumina-content, and protected by U.S.A. Pats. 2,017,056, 2,019,208, and 2,019,209; (ii) "*Monofrax* H," of very pure material, one member consisting largely of α-alumina with about 2 per cent. of soda (see U.S.A. Pat. 2,043,029); and (iii) "*Monofrax* K," a varied group containing 80 per cent. or more alumina, 12 per cent. or more of chromic oxide, and more than 6 per cent. of iron oxide (U.S.A. Pat. 2,063,154). Under a pressure of 25 lbs. per square inch, a sample of *Monofrax* showed an expansion of 1·43 per cent. at 1500° C., but after being retained at that temperature for 1¾ hours the volume was reduced by only 0·12 per cent.

Uses.—Bricks and blocks of the Corhart and Monofrax types are particularly suitable for glass-melting tanks, lining the hot zones of rotary cement-kilns, various metallurgical furnaces, silicate of soda, and fritting furnaces, recuperators, and some boilers.

Fused alumina is also an important constituent of some kinds of refractory porcelain (see Chapter XVI.).

CHAPTER VI.

CARBON BRICKS.

CARBON bricks[1] appear to have first been made by Kast, in 1857, from a mixture of crushed coke and glue-water, but the first regular use of carbon bricks was in South France in 1876; in 1877 W. Weldon patented a method of manufacture which is still the most extensively used. Carbon bricks are valued on account of their high refractoriness, neutrality, electrical conductivity, and resistance to corrosion and abrasion. Valuable as they are, the demand is not great—no works can manufacture more than 6 tons a day without becoming seriously overstocked—so that few firms are engaged in their production. Reputation has a considerable effect on the sale, and many carbon bricks are sent from Rhenish Prussia to Russia, in spite of the fact that works in Silesia can deliver a similar article at a lower rate for carriage.

The manufacture is dirty and very unpleasant, so that only few workmen will undertake it, and these must be well paid.

Uses.—Firebricks made of carbon are used in the bottoms, sides, and boshes of furnaces employed in the iron and steel industries, the upper part or crown being built of stronger bricks made of clay or silica. Carbon bricks and slabs are used in furnaces for smelting copper, lead, and aluminium, and also in steel furnaces.

S. G. Thomas obtained a British patent in 1878, in which he specified the use of carbon bricks as a neutral, intermediate course between basic and acid courses in furnaces and converters, and in the United Kingdom the use of carbon bricks is largely confined to this purpose of keeping basic and acid bricks out of contact with each other. In several German ironworks, it has been found profitable to line the whole of the lower part of the blast furnaces with carbon bricks, the shaft above the tuyères being built of fireclay bricks.

The advantages claimed for the employment of carbon bricks are the lessened oxidation of the metal in the furnace and the longer life of the furnace.

Carbon bricks have proved very valuable for furnaces using grey iron which is saturated with carbon. For white pig-iron and other metals, where a less proportion of carbon is present, such bricks are not so suitable, as they tend to give up carbon to the metal, and are thereby destroyed. Carbon bricks are not usually suitable for those parts of a furnace which are continuously in contact with molten iron, but for lead furnaces they have proved excellent. They are employed in electric furnaces used in the manufacture of aluminium, etc. Carbon bricks are increasingly used for lining paper-pulp digesters and metal-pickling tanks.

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[1] Also known as *coke bricks.*

Materials.—The chief constituent of carbon bricks is, as the name implies, some form of carbon, the one usually employed being crushed blast-furnace coke, containing not more than 8 per cent. of ash, but it is necessary to test all cokes proposed to be used, as the quality of the finished bricks largely depends on that of the raw material. Some cokes are quite unsuitable for carbon bricks, as, in addition to a low content of ash, it is necessary that the coke shall have a high mechanical strength. The best coke is in large, light pieces ; small coke is often too friable and contaminated with clinker, so that bricks made of it would crack in use.

The use of charcoal has also been suggested, but this material has not been used extensively. Bricks containing less than 30 per cent. of graphite or coke, and known as *plumbago bricks,* are described on p. 394.

The *bond* used in carbon bricks is almost invariably *gas-tar* or soft pitch, which has been freed from ammonia and light oils by distillation. Care must be taken that the distillation has not removed the heavier oils to which the tar owes its binding power. It is advisable to " boil " the tar well before use, but not to let it get too stiff ; some manufacturers of carbon bricks " boil " part of the crushed coke in the tar.

A. T. Hinckley has suggested the use of *colloidal carbon* as a bond, especially for uniting particles of graphite.

Among other bonds which have been suggested are (*a*) *fireclay* (patented in 1882 by F. C. Glacer), (*b*) *water-glass* or silicate of soda (patented by S. G. Thomas in 1878), and (*c*) *milk of lime* (patented by E. H. and A. H. Cowles in 1886), or a mixture of this material with pitch or tar (patented by H. Hartenstein in 1906). None of these bonds can be regarded as of commercial importance at the present time.

Preparing the Materials.—The coke used should have as low a percentage of ash as possible. It should be crushed in an edge-runner mill or a ball mill to particles of $\frac{1}{25}$ to $\frac{1}{12}$ inch in diameter, and stored in a dry and warm place. It is not considered necessary to grade it carefully, though this would be an advantage.

Mixing.—A suitable quantity of the warm, dry coke is weighed, and spread in a thin layer on a clean floor. The desired amount (usually one-quarter of the weight of the coke) of hot fluid tar or melted pitch is poured over it and the two are mixed by means of shovels. Not more than 5 cwt. can be mixed at a time, as the bond soon chills and forms balls from which a uniform paste cannot be produced. The use of a heated floor is unsatisfactory, as it causes the evolution of unpleasant vapours from the tar. The mixing must, therefore, be effected as rapidly as possible.

It is advantageous to pass the roughly mixed materials through a pug mill provided with a steam-heated jacket or with a double casing, which can be heated by a small coke fire placed beneath the mill.

The mixing must be sufficiently long, and at such a temperature, that the extruded paste is of uniform texture, with no irregular lumps or nodules and no fissures. These, if present, are due to insufficient mixing, or to the temperature being too low and so causing the tar to solidify.

Making.—Carbon bricks are usually made in iron or wooden moulds[1] provided with a separate base-board.

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[1] As the cost of moulding large blocks is proportionately less than that of bricks, some firms prefer to make blocks 18 inches by 9 inches by 6 inches rather than bricks. The shrinkage in burning does not exceed 1½ per cent., so there is little need to allow for it. The bricks may, however, be made rather thicker than required, so as to allow of their being dressed when in the furnace.

A sheet of paper is laid on the base-board or pallet; the inside of the mould is brushed over with paraffin or crude oil, and the mould is placed on the base. Sufficient paste is then thrown in the mould to occupy about one-quarter of it, and this material is then tamped thoroughly with hot iron stamps (fig. 107), filling the corners completely. Unless the tamping is done well, the bricks will be weak and too porous. When it is necessary to add more material, the upper surface of that in the mould is roughened with a comb, a fresh quantity of paste is added and the tamping is repeated as before. These operations are combined until the mould is more than completely filled.[1] Any superfluous material is cut off with a palette knife, and the surface is smoothed with a well-oiled iron strike or straight-edge.

As soon as the brick is sufficiently cool, the mould is removed and the brick, on its base-board or pallet, is taken to the hardening shed.

Where the output is sufficiently large, the bricks may be made in a press of the type shown in fig. 53.

Hardening.—The hardening room should be thoroughly well ventilated and kept cool. All heat—even that of the direct rays of the sun—must be avoided, as it would soften the bricks. They must also be protected from frost. Small pieces may be sent to the kiln after a few hours, but bricks and larger blocks should be allowed two or three weeks to harden.

Setting.—Carbon bricks or blocks are very tender and must be handled with great care. They must be set uniformly, as any irregularity in their bearing will cause them to crack, and may make them fall to pieces. For this reason, it is desirable to " bed " these bricks in a layer of coke-dust.

The setting is a slow process and requires both care and skill. If the kiln is warm, the bricks must be placed rapidly or they will fall. If ordinary kilns are used, the bricks can only occupy about one-tenth of the total capacity of the kiln. The portions of the kiln not occupied by carbon bricks are usually filled with fireclay bricks.

The bricks are set in small cupboards, the spaces between the bricks being filled with sand, or a mixture of sand and powdered coke. The top row of bricks in each compartment should be covered with an 8-inch layer of sand and coke.

Some manufacturers prefer to set the bricks in saggers, the latter being then filled completely with coke-dust and luted with clay-paste. Other manufacturers bake the bricks in the iron moulds in which they are made.

When the kiln has been filled with the bricks to be burned, it must be closed tightly and all crevices daubed with lean clay paste so as to prevent all access of air into the interior. Any air which comes into contact with the bricks during the burning will partly destroy them, as carbon bricks will burn if heated in contact with air.

Kilns.—Single down-draught or Newcastle kilns may be used satisfactorily for burning carbon bricks, but if there is a sufficient output, it is better to construct a special kiln of the continuous chamber type, with indirect firing, and of such a design that each small chamber is completely surrounded by fire-flues, the whole being worked in a similar manner to a Hoffmann or a Mendheim kiln built on a small scale with a limited air-supply.

Larger continuous chamber kilns are also well adapted for burning carbon bricks, as they permit the ready erection of " cupboards " and other arrangements for protecting the bricks from direct contact with air and hot kiln gases. Continuous muffle-kilns are better than open kilns.

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[1] The amount of material put into the mould must be more than sufficient to fill it, even after tamping.

The output of a tunnel kiln is usually too large for such a kiln to be employed for carbon bricks, otherwise this type of kiln is quite suitable.

Burning.—Carbon bricks require to be heated to a temperature sufficient to coke the tar bond and to form hard bricks. To effect this, the firing of the kiln is conducted in the usual manner, but special care is needed, as the bricks are very soft at temperatures between 30° C. and 250° C., after which most of the tar is converted into coke and the bricks then begin to harden. The heating is continued until a dull red heat is reached. This is maintained for two or three days, after which the kiln is allowed to cool slowly. Opinions differ widely as to the minimum temperature at which carbon bricks can be burned, but it is generally acknowledged that if Seger Cone 10 (1300° C.) is fully bent, the bricks will have had ample heating. Some firms never allow their bricks to attain this temperature, but finish them at 1000° C. to 1100° C. There is no doubt that this is much too low for the production of really strong coke bricks.

If the greater part of the kiln is occupied by fireclay bricks—the carbon bricks being placed in muffle-like boxes, which protect their contents from the action of hot air—the burning of the kiln may be carried out in exactly the same manner as that of ordinary firebricks.

Cooling.—The kiln is allowed to cool in the usual manner, but it should not be opened until it is too cool for the carbon bricks to be oxidised or to set themselves on fire.

About ten days are usually required for burning and cooling a kiln containing coke bricks.

Emptying the Kiln.—The door is carefully removed and the carbon bricks are taken out, one at a time, and stored in a closed shed. They should not be exposed to draughts or currents of air.

The coke-dust used for packing the bricks in the kiln is sifted so as to remove lumps, and the powder is used for bedding the next lot of bricks to be burned.

Before sending the carbon bricks away, they should be examined and all adherent coke-dust should be removed. Defective bricks are sent to the mill and re-ground.

Some makers dip the bricks into hot tar so as to give them a smooth surface and to hide any small fissures and cracks which may be present.

Properties.—Firebricks made of coke should be light grey, both inside and out, and should emit a clear, ringing sound when struck. They should have plain and even faces, with sharp arrises and corners, so that there may be the thinnest possible joints between the bricks. Friable or "soft" corners and arrises should be regarded as defects, and probably indicate insufficient tamping during moulding.

When a brick is broken and the fractured face is examined, it should be free from fissures and cracks.

The *specific gravity* of coke bricks lies between 1·5 and 1·9 and varies with the amount of ash in the bricks.

The *percentage of ash* in coke bricks varies greatly; it is seldom under 7 per cent., but should not exceed 14 per cent.

The *crushing strength* should be at least 4500 lbs. per square inch.

K. Endell[1] has found that carbon bricks, under a load of 40 lbs. per square inch, did not soften below 1700° C.

The *refractoriness* of coke bricks cannot be stated in figures, as, if properly made, they do not lose their shape at any attainable temperature. When

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[1] *Ber. deut. ker. Ges.*, 1921 (ii.), 73.

exposed to air and heated strongly they gradually burn away and, for this reason, the exposed face of carbon bricks must be protected from air and abrasion by a coating of fireclay or slag or by a " facing" of firebricks.

Carbon bricks are insensitive to sudden changes in temperature, are not readily attacked by slags, and are remarkably constant in volume when heated. They have a fairly constant thermal conductivity of about 0·0012 gramme calories per c.c. per second per 1° C.

The specific heat of carbon bricks varies considerably; at a temperature of 200° C. the specific heat is 0·312, whilst at 1000° C. it reaches 0·412.

In most works where they have been used, carbon bricks have given great satisfaction, but in a few cases they have proved failures. No complete explanation of this has yet been given.

The objections raised to the use of coke bricks some years ago do not apply to the better qualities now made. It is, however, important that after being laid in position in the furnace they should be coated with fireclay cement or with repeated coats of water-glass or even with thin fireclay slabs, so as to protect them from the air whilst the furnace is being heated.

Graphite and Plumbago Bricks.

Graphite and plumbago bricks are described on p. 394.

Carbon Electrodes.

The electrodes used in electric furnaces require to be highly refractory.

Such electrodes are made of coke, charcoal, anthracite, retort-graphite, pitch, petroleum coke, and either natural or artificial graphite.[1] They must contain as low a proportion of ash as possible—certainly less than 3 per cent.—and must be quite free from particles of metal. One or more of these materials is first heated to redness to remove readily volatile matter and gases, and when cool it is ground to powder. For some purposes, a grain size of 0·08 to 0·12 inch is preferred, but for others a finer powder is more suitable.

The powder is sieved to ensure correct grading, and is then mixed with 10 to 30 per cent. of dry tar, or preferably a mixture of tar oil and pitch in accurately adjusted proportions. A steam-heated pug mill is the most convenient form of mixer.

The electrodes are shaped in iron moulds by hydraulic pressure, the best results being obtained when the moulds are steam-heated to a temperature of 40° C. to 90° C. Alternatively, the plastic mass may be extruded through a mouthpiece as in the manufacture of wire-cut bricks, except that a much greater pressure (350 to 360 tons per square foot) is required.

After moulding, the electrodes are allowed to harden for several days before being burned. They may be burned in an electric furnace or in a gas-fired kiln. The electric furnace is rectangular in shape, and consists of four walls, two of which are connected to the source of electricity. The electrodes are placed on one another in the furnace, the space between them being filled with a suitable coke. On switching on the current, the electrodes act as the resistor in the furnace, and become gradually hotter and hotter, until they attain a temperature of 1100° C. to 1500° C., and this temperature is maintained until all volatile matter has been expelled and the electrodes are thoroughly fired. If the furnace is a large one, the firing may require a fortnight, and the

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[1] Titanium oxide (rutile), magnetite, chromium oxide, cryolite, fluorspar, or other fluorides, sulphur, and various other substances are sometimes added.

cooling three weeks. Only a low voltage (about 60 volts) is employed, but the amount of current is necessarily large.

The gas-fired kilns used for burning electrodes consist of a series of rectangular chambers, with heating flues along the sides and bottom. Each chamber works independently of the others, some being heated, whilst others are cooling or being filled or emptied. The burning occupies about a week, the temperature not exceeding 600° C. during the first five days, after which it is raised fairly rapidly to about 1100° C., and maintained at this temperature for the remainder of the burning period. The chamber and its contents are then allowed to cool very slowly, so as to anneal the electrodes thoroughly.

Whichever kind of furnace or kiln is used, the burning must be skilfully controlled, as the electrodes crack and fall to pieces if too rapidly heated during the early stages of the burning.

The disadvantage of electric furnaces for firing electrodes is that they are costly and difficult to control. Gas-fired furnaces have the advantage that the volatile matter evolved during the burning may be collected, and the kilns themselves work regeneratively, so that relatively little heat is wasted. Gas-fired electrodes are much more easily cleaned than those which have been electrically heated. For these reasons, gas-fired kilns are increasingly used, and are superseding the electric ones.

The electrodes are cleaned, either by brushing them with wire brushes, or by tumbling them in a steel barrel. If necessary, an emery wheel may be used to complete the dressing. When properly made, carbon electrodes are hard and dense, with a fine, close texture; if sound and well-burned, they ring like a bell when struck. Their specific gravity varies from 1·88 to 1·98, whilst the apparent density should be 1·5 to 1·55, which is equivalent to 93·5 to 96·5 lbs. per cubic foot. The electrical resistivity is inversely proportional to the specific gravity.

The crushing strength of carbon electrodes should be 3200 to 5850 lbs. per square inch, and the modulus of rupture 700 to 1200 lbs. per square inch.

CHAPTER VII.

BRICKS MADE OF CHROMITE OR IRON ORE.

EXCEEDINGLY valuable, though costly, bricks of a neutral character are made from chromite—an ore containing about 50 per cent. of chromic oxide and 25 per cent. of iron oxide. Similar, but less durable, bricks are made from several kinds of iron ores and residues.

CHROMITE BRICKS.

Uses.—Chromite bricks were first used in open-hearth furnaces in 1879, and though they have since been used extensively as a neutral course between basic and acid bricks in steel furnaces and converters and in furnaces for smelting copper, antimony, and tin,[1] it was the use of bricks made of chromite and magnesia which showed the true value of chromite.

Materials.—The chrome ore used is generally of low grade, as the cost of the better qualities is regarded as prohibitive (see Table LI., p. 201). Chrome-iron ore which is free from silica cracks and becomes friable when heated because it lacks the necessary binding agent. This defect is avoided by the use of an appropriate bond. More than 8 per cent. of silica is objectionable.

Instead of using chrome ore alone as the chief constituent, bauxite may be added in suitable proportions, the mixture calcined and then mixed with a suitable amount of dead-burned magnesite so as to form a mixture of spinels and mullite.

Alternatively, the composition of the chrome ore may be " corrected " by adding suitable proportions of magnesia (with or without alumina) so as to produce the maximum amount of spinel (see " Spinel Bricks " and " Chrome Spinel Bricks," pp. 508 and 529).

The most suitable treatments for chrome ore rich in silica are:

(i) To adjust the composition as nearly as possible to 80 per cent. of silica and 20 per cent. of chromium oxide and to keep the lime compounds at a minimum.

(ii) To add magnesia so as to produce a mixture of magnesium chromite and forsterite.

A mineral from which excellent refractory bricks are being produced is *picotite*, with the reputed formula $(Mg,Fe)(Al,Fe,Cr)_2O_4$. These bricks are highly resistant to spalling; they absorb slag, but leave a dry surface, so that the molten metal and slag do not adhere to each other.

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[1] In French antimony works the greater part of the furnaces is lined with chromite bricks; in French tin works they are used for the bottom and sides of the hearth. E. Hall prefers *lumps* of chromite bedded in a mixture of crushed chromite and blende, and regards them as more durable than bricks.

The following *bonds* are, or have been, used:—

(*a*) *Clay*, in the form of fireclay or kaolin, is generally satisfactory. The use of clay with a little resin, coal, or other carbonaceous matter was patented by J. Bach in 1903. The objection to fireclay is that it produces bricks which fuse at a notably lower temperature than chromite bricks bonded with lime.

(*b*) *Lime*—usually in the form of milk of lime, as patented by W. J. A. Donald in 1885—is satisfactory if used in an amount equivalent to about 5 per cent. of the weight of the bricks.

(*c*) *Plaster of Paris* forms lime when burned at a sufficiently high temperature. In the earlier stages of manufacture its bonding properties are useful, though the sulphur it contains is always objectionable.

(*d*) *Bauxite* as a bond was patented by W. J. A. Donald in 1885. Lynam and Rees[1] found that the addition of alumina to chrome bricks increased the tensile strength at high temperatures and also the compressive strength, but reduced the thermal expansion and the tendency to spalling.

(*e*) *Magnesia* or *magnesium carbonate* in the proportion of 5 to 10 per cent. of magnesia (or double this quantity of carbonate) was patented by J. Imray in 1885. The use of 12 per cent. of *dolomite* as a bond was patented by K. A. Mankau in 1912, his idea being to form a polybasic spinel (see p. 469; also p. 235). In T. Twynam's (1915) patents it is claimed that a mixture of magnesite with half its weight of chromite does not shrink at 1600° C. *Magnesium chloride* is used as a bond in some French works.

(*f*) *Tar* (patented by J. H. Darbyshire in 1881) or *small coal* (patented by J. Imray in 1883 and by M. Weissbein in 1899). The tar is used whilst hot; the mixture of ore and small coal must be heated in a rotary furnace so as to convert some of the coal into tar before the material can be made into bricks.

(*g*) *Chromium salts*, particularly potassium bichromate (patented by T. Twynam in 1886), or the light oxide formed by calcining chromium salts (patented by P. E. Placet in 1896).

(*h*) *Alkaline salts*, especially sodium or potassium, carbonates, hydroxides, silicates or chlorides (patented by T. Twynam in 1886).

Iron oxide cannot be used as a bond because it makes chromite bricks containing it crack and disintegrate. To some extent silica inhibits this harmful action.

Of these bonds the most usual are (*a*) and (*b*), but (*e*) offers great possibilities, as it can form forsterite and chrome spinel, both of which have exceptional binding power. It can also form a bond with some of the other impurities in the chrome ore.

The addition of 2 to 8 per cent. of silica or of alumina to a chrome ore has been found[2] to increase the toughness and strength of the bricks without reducing the resistance to slag (see "Chrome-Silica Bricks," p. 530).

Chromite bricks have been made without any added bond, some of the chromite being ground to flour and then added to the ordinary ground chromite. In such bricks, the bond is formed by the action of the impurities (such as serpentine) which are present.

Preparing the Materials.—With the exception of bond (*f*), the powdered ore and bond are mixed with sufficient water to make a stiff paste, this being effected in a trough mixer. Some manufacturers prefer to mix the dry bond and ore, and to sift the mixture through a coarse sieve before mixing with water. When tar is used as a bond, it is heated until sufficiently fluid, and is

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[1] *Trans. Cer. Soc.*, 1937, **36**, 110, 133.

[2] Lynam and Rees, *Trans. Cer. Soc.*, 1936, **35**, 165; 1937, **36**, 110–172.

used in a manner similar to that employed in the manufacture of carbon bricks (Chapter VI.).

In some cases the ground chrome ore is mixed with 10 per cent. of milk of lime and tar in an edge-runner mill, moulded into rough blocks, and burned at the highest available temperature. The crude bricks are then ground, mixed with the smallest practicable proportion of milk of lime and tar, and are then moulded into bricks.

Moulding may be done by hand in iron moulds, the mould being filled in several portions, each of which is well tamped before the next is added. Some manufacturers prefer to use hot moulds, though these are not really necessary. Others prefer to use a press such as one of those shown in figs. 51–53.

Drying[1] must be very gradual, but is not particularly difficult. The bricks may usually be placed on a warm floor, the temperature of which is slowly increased. After twelve hours, the drying may be more rapid. Care must be taken to make the drying complete, as imperfectly dried bricks fall to pieces in the kiln. Chromite bricks may be dried quite satisfactorily in tunnel dryers.

Burning.—Chromite bricks may be burned in any type of kiln suitable for firebricks. The final temperature should not be less than 1460° C. (Seger Cone 16), and may advantageously be considerably higher (1700° C.). It is usual to burn chromite bricks simultaneously with silica bricks. Chromite bricks must be burned very carefully, as if the speed of burning is too great they may swell and be spoiled. They should be placed high up in the kiln so as not to be subjected to much pressure.

Properties.—Chromite bricks usually contain about 33 per cent. of chromic oxide. The better qualities contain between 35 and 65 per cent. of chromic oxide and less than 6 per cent. of silica.

Three analyses of chromite bricks are given below. Samples A and B are much richer in chromite than the majority of chromite bricks; C has about the average composition.

TABLE LXXXIV.—ANALYSES OF CHROMITE BRICKS.

	A.	B.	C.
Silica	1·74	2·42	5·23
Chromic oxide	51·43	62·16	35·87
Iron oxide	35·54	28·02	15·26
Alumina	2·05	2·51	31·28
Magnesia	3·84	0·82	11·43
Lime	5·27	3·95	0·91

Chromite bricks consist essentially of (i) chromium oxide in the free state, (ii) iron oxide, partly in the free state and partly as fayalite and other iron silicates, (iii) chrome spinel—the amount depending on that of the lime and magnesia present—and (iv) a complex glassy matrix (composed of magnesium silicates and other silicates) which unites the other, more refractory, materials. If much magnesia has been added, forsterite and magnesio-ferrite may also be produced. When a large proportion of magnesia is present, only that in the form of magnesium chromate is refractory; the remainder combines with any silica, alumina, and ferrous oxide present to form a fusible glass or matrix.

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[1] Bricks made with tar or small coal are not dried.

On cooling a fused chrome ore containing more than a small proportion of silica, the chrome compounds are the first to crystallise out of the siliceous melt, and thus account for much of the refractoriness of chromite bricks. More than a very small proportion of lime is objectionable, as it greatly reduces the refractoriness.

As most of the silica in plain chromite bricks is in the form of cristobalite, these bricks are often very sensitive to changes in temperature, and are particularly liable to crack when cooled to 200° to 300° C.

An excess of silica in chromite bricks reduces the refractoriness-under-load and greatly shortens the time between the first signs of distortion and complete collapse of the test-piece.

Chrome bricks resist both basic and acid slags, but are sensitive to reducing conditions and to sudden changes in temperature.

Refractoriness.—Chromite bricks are highly refractory; the melting-point of several samples examined by C. Kanolt was 2050° C. This figure is notably higher than that obtained by the author in the course of his professional practice, the chromite bricks examined by him having softening-points varying from 1680° C. to 1850° C. They cannot be heated, when in use, to a temperature much exceeding 1500° C., as above this temperature they tend to disintegrate. Clay-bonded chromite bricks are less resistant to heat than those in which lime is used, the average refractoriness of the clay-bonded bricks being 1700° C., whilst that of the lime-bonded bricks was above 1850° C.

The refractoriness of chromite bricks depends on the proportion of chromic oxide present, the pure oxide being practically infusible; the cost of the purer ores prevents their being used for bricks.

The *refractoriness-under-load* of chromite bricks is 1400° to 1550° C. with a pressure of 50 lbs. per square inch, but that of many commercial chromite bricks is only 1450° C. This is partly due to chromite softening many degrees below its melting-point. The effect of free silica on the refractoriness-under-load may be serious (see *above*).

The addition of 20 to 40 per cent. of spinel ($MgO.Al_2O_3$) increases the refractoriness considerably. A still greater increase is obtained by adding magnesia to produce forsterite, $2MgO.SiO_2$, which has a melting-point of 1910° C. as compared with 1590° C., the melting-point of enstatite, $MgO.SiO_2$. Alternatively, lime may be used with magnesia to form $2CaO.SiO_2$ (m.pt. 2130° C.) or $CaO.MgO.SiO_2$ (monticellite, m.pt. 1620° C.).

Mechanical Strength.—Both in the cold and when heated, chromite bricks have a mechanical strength of 200 to 400 kg. per square cm. (180 to 360 tons per square foot). The lower figure corresponds to that for magnesia bricks, but by very careful manipulation and the use of suitable ores, chromite bricks with almost double the strength of magnesia bricks may be made. Like magnesia bricks, those made of chromite fail suddenly when heated to 1450° C. under a load of 50 lbs. per square inch. V. Bodin found that the strength of chromite bricks diminishes rapidly when they are heated to temperatures above 900° C. (see fig. 109).

The strongest bricks tested are those of chrome ore alone (without a binder), the next strongest with about 14 per cent. of clay, and the remainder with lime as a binder. Lime is not a suitable ingredient of chromite bricks when more than 5 per cent. is present, and, notwithstanding the difficulties created by the shrinkage when clay is used as a binder, it appears to give the best results.

The transverse strength of chromite bricks was found by Hartmann and

Köhler[1] to be 1390 lbs. per square inch at 20° C., and only 22 lbs. per square inch at 1350° C.

The *electrical resistivity* of chromite bricks as determined by Hartmann, Sullivan, and Allen,[2] Stansfield, M'Leod and M'Mahon, and H. E. White[3] are shown in Table LXXXV. These great differences have not been explained.

The *thermal conductivity* of chromite bricks is very low,[4] viz. 0·0040 g.-cal./cm./° C./sec.

The *reversible expansion* of chromite bricks is high, up to 1200° C. (approximately equal to the expansion of silica). At higher temperatures shrinkage occurs, and the original volume is restored at about 1350° C.[5]

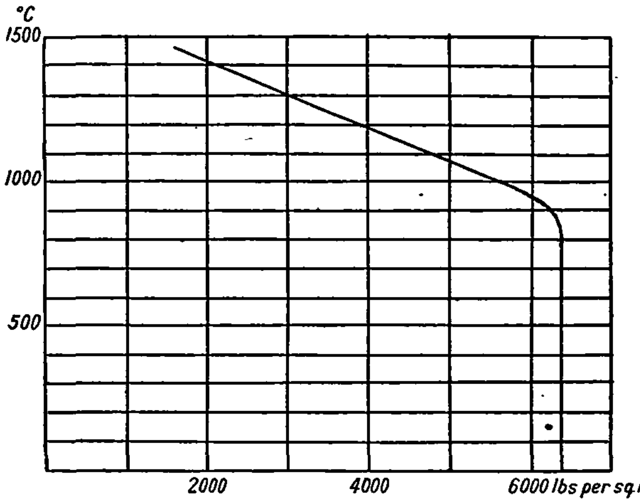

FIG. 109.—Strength of chromite bricks (V. Bodin).

The *porosity* of chromite bricks is usually about 14 per cent. by volume but varies greatly in bricks from different sources. If it is reduced by very prolonged heating, the bricks tend to spall.

The *apparent specific gravity* of chromite bricks should be 3·8 to 4·0 ; if lower it indicates an excess of silica or insufficient burning of either the chrome ore or the bricks.

Resistance to Slags.—Chromite bricks are less resistant to blast-furnace slags than to slags from acid open-hearth steel furnaces.

Basic slags and most fluxes do not attack chromite bricks, but they can be decomposed slowly by bisulphate of soda. Acid fluxes attack chromite bricks very slightly.

Oxidation and Reduction.—Chromite bricks are not oxidised by air. When heated in intimate contact with carbon or with reducing gases at very high temperatures, ferro-chrome is formed as a reduction product.

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[1] *Trans. Amer. Electrochem. Soc.*, 1921, **40**, 457.

[2] *Ibid.*, 1920, **38**, 279.

[3] *J. Amer. Cer. Soc.*, 1932, **15**, 598–1610.

[4] F. H. Norton, *J. Amer. Cer. Soc.*, 1927, **10**, 30–52.

[5] For further information on thermal expansion, see Rigby and Green, *Trans. Cer. Soc.*, 1938, **37**, 389.

TABLE LXXXV.—ELECTRICAL RESISTIVITY OF CHROMITE BRICKS (OHM-CMS.).

Temperature, °C.	Hartmann and Co-workers.	Stansfield and Co-workers.	Norton.
cold	48,000,000	..	..
300	..	..	51,000
400	..	..	8,850
500	..	..	4,480
600	..	..	1,760
700	..	..	1,290
800	803,000	2800	815
900	525,000	..	430
1000	171,000	..	240
1100	78,000	..	89
1200	63,000	..	53
1300	77,000	..	43
1400	85,000	320	..
1500	41,000	..	..

Shrinkage.—Chromite bricks tend to shrink excessively unless a fairly large proportion of magnesia is present (see *below*). The shrinkage of the bricks is due to that of the chromite and to the formation by silica of compounds with the various oxides present with the exception of chromic oxide, which does not combine with silica. The greater part of the shrinkage should occur during the burning in the course of manufacture, but it is also marked when imperfectly burned bricks are used.

Expansion.—The linear thermal expansion of chromite[1] bricks between "cold" and 1500° C. is 1·70 per cent. It increases progressively from 0·016 at 20° C. to 0·104 at 400° C., and more rapidly to 0·780 at 1000° C.; above this temperature a marked increase in expansion occurs and continues up to 1200° C., when the expansion is 1·188 per cent.; it then increases more slowly, being 1·678 at 1400° C. and 1·700 at 1500° C. According to B. Bogitch (fig. 105) it increases regularly from "cold" to 1500° C.

The expansion can be reduced by the addition of clay. The expansion under reducing conditions is much greater than under oxidising ones.

Spalling.—Chromite bricks have a moderate resistance to spalling. This resistance is much greater when magnesia is present (see "Chrome-Magnesia Bricks" and "Chrome Spinel Bricks").

CHROME-MAGNESIA BRICKS.

It was known as long ago as 1910 that the addition of magnesia to the materials used for making chromite bricks greatly improved the quality, and Chesters and Parmlee[2] found that this improvement and a great reduction in the shrinkage are due to the formation of forsterite.[3] The maximum compensation occurs with a mixture containing 20 to 25 per cent. of chromite and 75 to 80 per cent. of magnesite, but X-ray and microscopic examination have shown that only part of the magnesia reacts. The forsterite is produced by adding a suitable proportion of silica to the chrome-magnesite mixture and burning the bricks for a longer period than usual. Alternatively, talc may be

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[1] Heger, Sonntag, and Leineweber, *Stahl u. Eisen*, 1935, **55**, 265–271.

[2] *J. Amer. Cer. Soc.*, 1935, **18**, 94.

[3] See Eng. Pat. 409,130 (1932).

used instead of silica, provided rather less magnesia is employed. The substitution of felspar for silica produces bricks of low strength at high temperatures.

The method of manufacture is the same as for chromite and magnesite bricks, except that the raw material is not always pre-calcined. The importance of the grading is emphasised in Eng. Pats. 435,448 (1933) and 456,207 (1936).

The best commercial chrome-magnesite bricks are of two kinds: (i) chrome-magnesia bricks, and (ii) chrome spinel bricks; the latter are described on p. 529. The difference is largely in the proportion of the chromic oxide and magnesia present and in the heat-treatment, *i.e.* in the extent to which chrome spinel is formed.

Chrome-magnesia bricks are made of a mixture of about 25 per cent. of magnesite and 75 per cent. of chromite, but one British firm supplies bricks of this kind containing only 10 per cent. of magnesite.

A well-known Austrian brick contains magnesia 44, iron oxide 11, chromic oxide 30, and silica 11 per cent. A German brick almost equally popular contains magnesia 31, iron oxide 13, chromic oxide 36, and silica 7 per cent. The chief constituent in both is a dark isotropic mineral with a refractive index of 2·05.

Bricks which are specially resistant to changes in temperature are made of a mixture of chrome ore 10 to 30 parts, corundum or other form of alumina (in the form of fine meal) 4 to 7 parts, magnesite (fine meal) 0 to 25 parts, magnesite (coarse meal) 45 to 60 parts and, if necessary, a binder (Eng. Pat. 468,456—1936).

A chromite material said to be of unusually high refractoriness is made by heating a mixture of chrome ore and magnesia until all the low-melting gangue is transformed into forsterite. The product is granulated, plasticised, shaped and fired at above 1650° C. (Eng. Pat. 468,659—1936).

Bricks made of a mixture of magnesite and chrome ore and a ferro-chrome slag[1] so as to produce a composition of slag 30, magnesite 20 to 40, and chromite 30 to 50 per cent. had a refractoriness of 1920° C., a refractoriness-under-load of 1450° C., porosity 28·7 per cent., sp. gr. 2·52, and great resistance to thermal shock.

The best chrome-magnesia bricks have a high resistance to spalling and a high refractoriness-under-load[2] (1700° C.), but to ensure this the grading must be suitable and the magnesite must consist wholly of small particles, whilst the chromite particles must be coarse (see Eng. Pat. 435,448).

Properties.—In chrome-magnesia bricks of good quality the average chromium-oxide content is 18 to 20 per cent. The spinel content is about 84 per cent. The silica should not exceed 8 per cent. or the bricks will spall and not resist slags.

Such bricks have: (*a*) a high refractoriness-under-load,[3] *i.e.* 1500° to 1600° C.; (*b*) a great resistance to spalling; (*c*) a constant volume (or slight expansion) after re-heating and cooling; (*d*) a zero after-contraction after heating for 2 hours at 1500° C.; (*e*) a mean coefficient of thermal expansion (linear) of 9×10^{-6} per degree C., or 1·35 per cent. between cold and 1500° C.; and (*f*) a thermal conductivity of 0·0041 g.-cal./cm./° C./sec., which is lower than that of magnesia bricks.

The specific gravity is about 3·8, the volume-weight 3·89 when cast and

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[1] Tereschenko, *Ziteïn-Tech. So.*, 1937, **27**, 1239.

[2] Chesters and Lee, *Trans. Cer. Soc.*, 1937, **36**, 304.

[3] The refractoriness-under-load varies greatly; the reason is not known.

3·16 when pressed. The resistance to thermal shock of the cast bricks is not very great.[1] Tests in a steel-works furnace show that such bricks can last twenty times as long as silica bricks.

A brick which is claimed to be more resistant to spalling than any other consists of coarse chrome ore and fine magnesia and lime (Eng. Pat. 381,981—1931) in which the bond consists essentially of dicalcium silicate containing a little chromium oxide, which stabilises it. The silica is derived chiefly from the chrome ore, and the magnesia-lime refractory may, advantageously, consist of sufficient dicalcium silicate to form a bond with as much magnesia as is naturally associated with that proportion of lime in the dolomite used.

Chrome-magnesia bricks tend to combine the good qualities of the non-spalling kinds of magnesite bricks with those of chrome bricks without having the bad qualities of either. They are reasonably resistant to thermal shock and all slags, and they have a low after-contraction.

These bricks replace silica bricks in the roofs and arches of open-hearth furnaces and greatly increase the life of the latter.

Chrome-magnesia bricks tend to swell and " burst " when in contact with ferruginous slags, as a result of magnetite being absorbed by the chromite and also of the reaction of ferric oxide with magnesia forming magnesio-ferrite, $MgFe_2O_4$.[2] As magnesio-ferrite has a much lower refractoriness than chromite and spinel its formation is objectionable.

In a reducing atmosphere, chrome-magnesia bricks slowly collapse if heated to 1500° C. and maintained at that temperature, but the disintegration of chromite bricks is less due to the state of oxidation of the iron than to the absorption of iron by the material, followed by the growth of spinel crystals. Bricks made of fused spinels disintegrate more seriously than those of graded material.[3]

A. E. Dodd[4] has shown that for the maximum refractoriness-under-load the alumina should not exceed 8 per cent., the chromic oxide and magnesia should be present in equal proportions, and that variations from 3 to 9 per cent. of silica and 10 to 20 per cent. of iron oxide are not serious.

Unfortunately, Dodd also found that chrome-magnesia bricks, when maintained at 1500° C. under a pressure of 50 lbs. per square inch for five hours, showed a serious subsidence, so that such bricks are not suitable for furnace roofs. There appears to be no relation between the refractoriness-under-load (standard test) and the behaviour of the bricks when heated under a maintained temperature of 200° C. less than that corresponding to the refractoriness-under-load[5] test.

Uses.—Chrome-magnesia bricks are used in open-hearth steel furnaces (both basic and acid) as a support for the hearth, for the side walls, and, sometimes, for the roof. They are particularly suitable for the front and back walls and for the ports and hearths of open-hearth furnaces. They are also used for soaking pits and reheating furnaces, and for electric basic furnaces. They increase the output and save fuel.

In roofs and side walls of basic open-hearth furnaces they give a service superior to silica bricks, but are subject to a peculiar deterioration of the surface with spalling at a depth of 1 to 1½ inches. This appears to be due to the formation and growth of crystals of enstatite, $MgSiO_3$, surrounding globules of magnesio-ferrite in the ground-mass of orthosilicate (forsterite).

Iron oxide is absorbed by the hot face of the bricks, causing the chromite

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[1] *Ogneupory*, 1935, **8**, 594.

[2] *Trans. Cer. Soc.*, 1938, **37**, 285.

[3] *Trans. Cer. Soc.*, 1938, **37**, 343.

[4] *Trans. Cer. Soc.*, Preprint Nov. 1937.

[5] A. Dodd, *Brit. Clayworker*, 1937, **46**, 330.

to grow, whilst the matrix is converted into the more fusible magnesio-ferrite and magnesium metasilicate.

The strains set up by this growth cause disintegration of the surface and a movement backwards of the mobile matrix, and a layer ½ to 1 inch thick is formed. When the hot face is worn back, the temperature of the second zone is increased, liquefaction occurs, and a more serious breakdown of the surface occurs.[1]

Great care is needed when first heating an open-hearth furnace built with chrome-magnesia bricks, because in a reducing atmosphere at 800° to 1000° C. they expand 3 per cent.[2]

Unburned Bricks.—Chrome-magnesia bricks (*Ritex bricks*) containing 32 per cent. of magnesia, with sodium silicate or a temporary bond, can be used in an unburned state[3] for lining electric furnaces and for some other purposes.

In order to be satisfactory when in use, such unfired bricks must contain a chemical bond which will act as a lubricant during manufacture. The grading is important, 55 parts of coarse material and 45 parts of fine material being used and the intermediate sizes omitted. A great pressure is needed in shaping, and the grain-size must be carefully controlled so as to produce a very dense brick.

When well-made, with adequate attention to details, unfired bricks have ample strength, a high refractoriness-under-load and a high resistance to spalling.

R. Youngman (Eng. Pat. 250,480—1925) has suggested moulding a mixture of 60 per cent. of calcined magnesite, 35 per cent. of chrome ore, and 5 per cent. of sodium silicate, the bricks being dried but not burned. In 1934 the Veitscher Magnesiawerke A.G. (Austrian Pat. 137,672—1934) used sodium bisulphate instead of silicate and applied a pressure of 180 tons per brick. Such unfired bricks appear to be as stable in use as normal fired bricks.

CHROME-ALUMINA BRICKS.

E. N. Bunting[4] has found that the system Cr_2O_3–Al_2O_3 contains no definite compounds, the fusibility of mixtures rising steadily from 2045° C. with pure alumina to 2275° C. with pure chromium oxide.

Lynam and Rees[5] have found that the addition of alumina to chrome ore produces bricks of greater mechanical strength at high temperatures, with a more viscous bond, but a smaller temporary expansion. It also decreases spalling. The addition of more than 50 per cent. of bauxite reduces the resistance to slag. Owing to the presence of chromite, such bricks begin to soften at 1370° to 1400° C.

Bricks made of a mixture of chromic oxide (chrome ore) and alumina (bauxite) do not spall seriously and have a satisfactory refractoriness-under-load, but the total refractoriness is too low to make the bricks worth what they cost. If magnesia is added to a mixture of chromic oxide and alumina, the resistance to crushing when cold and to abrasion is seriously reduced. In other words, chrome-alumina bricks give poor results;[6] this is possibly due to the formation of ternary compounds, as there are no binary ones.

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[1] Hugill and Green, *Refract. J.*, 1938, **14**, 558.

[2] McKendrick, *Refract. J.*, 1938, **14**, 559.

[3] Eng. Pat. 350,480 (1925); also Hever, *Steel*, 1935, **97**, 22–25, 30; Trostel, *Iron Steel Eng.*, 1937, **3**, 27.

[4] *J. Res. Bur. Stand.*, 1931, **6** (6), 948.

[5] *Trans. Cer. Soc.*, 1937, **36**, 110–172.

[6] Lynam and Rees, *Trans. Cer. Soc.*, 1937, **36**, 133.

CHROME SPINEL BRICKS.

Bricks made essentially of an artificial chrome spinel ($2Cr_2O_3.MgO$ or $MgO.Cr_2O_3$) are superior in many respects to ordinary chromite bricks, particularly in having a greater refractoriness-under-load and a greater resistance to spalling. Some improvement is effected by merely mixing sufficient magnesia with the chrome ore (see " Chrome-Magnesia Bricks "), but much better results are obtained if chrome spinel is definitely the chief constituent of the bricks. One of the earliest attempts to produce chrome spinel bricks is the subject of Eng. Pat. 14,981 (1910), and since then the use of such bricks has rapidly increased.

At the present time chrome spinel bricks are chiefly made by mixing chrome ore and magnesia in suitable proportions, and burning the bricks under such conditions that chrome spinel (p. 200) is formed. If little of this substance is produced the bricks are more correctly termed " chrome-magnesia bricks." Hence, *unburned* bricks made of a mixture such as that described in Eng. Pat. 250,480 (1925) cannot be described as spinel bricks.

Lynam and Rees[1] recommend a mixture of 75 parts of chromite and 25 parts of magnesia, the whole of the magnesia being in " fine " particles (see also Eng. Pats. 456,207, 458,407, and 461,240).

Chrome spinel bricks are of two kinds:

(i) *Bonded bricks* are composed of ground chrome ore and magnesia with any of the bonds ordinarily used for chromite bricks (p. 521), or shaped without the use of a bond, by the application of a pressure of about 200 tons per brick to the slightly damp powdered mixture. In order to produce a sufficiently large proportion of spinel it is essential to burn the bricks for a long time at about 1500° C.

(ii) *Molten-cast bricks* are sometimes regarded as the only true chrome spinel bricks. Suitable mixtures of chrome ore and magnesite are fused in an electric furnace, and the molten mass is poured into iron or sand moulds and cooled very slowly.

One of the earliest bricks of this type, known as *siemensite*, is made of chrome ore, magnesite, and bauxite; the product is composed of 20 to 40 per cent. of chromium oxide, 18 to 30 per cent. of magnesia, 25 to 40 per cent. of alumina, and 8 to 14 per cent. of silica. These bricks contain more than 80 per cent. of spinel, about 10 per cent. of undetermined mineral, and only 2 to 3 per cent. of glassy material. They melt at above 2000° C., and under a load of 2 kg. per square cm. do not soften below 1800° C.

The refractoriness under a load of 2 kg. per square cm. is above 1800° C. The thermal conductivity is greater than that of magnesite. When siemensite is ground and pressed in an open mould it has a porosity of 15 to 20 per cent. and softens at 1500° to 1550° C., but the cast material has a porosity below 1·5 per cent.; it has a moderate resistance to spalling. Siemensite bricks require careful heating at 900° to 1000° C., but are very resistant to all slags. The linear thermal expansion up to 1200° C. is about 1·3 per cent. and is rather irregular.

The addition of 10 per cent. of talc to chrome-magnesia bricks and firing at 1560° C. produce bricks of great refractoriness-under-load, in which the forsterite is very uniformly distributed.[2]

The casting of molten spinel was patented in 1930 (Eng. Pat. 371,095) and in 1933 (Eng. Pat. 449,018) (see also Eng. Pats. 141,351—1920, 16,714—1906, 340,958, 409,315, 422,474, 448,941, and 448,942—1933).

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[1] *Trans. Cer. Soc.*, 1937, **36**, 137, 152.

[2] Lynam and Rees, *Trans. Cer. Soc.*, 1937, **36**, 152–172.

The production of magnesia-chromite bricks, containing not more than 80 per cent. of chromite, in which (i) the fine fraction (−0·1 mm.), (ii) the intermediate fraction, and (iii) the coarse fraction (+1 mm.) are in the ratios 20 to 40 : 15 to 25 : 35 to 65 (or in other specified proportions), the greater part of the magnesia being in the fine fraction, was patented in 1934 (Eng. Pat. 435,448).

The use of *slags* rich in chrome and magnesia for making bricks has also been patented (Eng. Pats. 302,087—1928, 324,312—1928, and 343,896—1929 are typical).

Uses.—Chrome spinel bricks are used for the same purposes as magnesia bricks, but are usually superior in quality where great resistance to slags is required. The distinction between chrome-magnesia bricks and chrome spinel bricks cannot be clearly defined, so that no definite comparison is practicable.

CHROME-SILICA BRICKS.

The term "chrome-silica bricks" is applied to bricks containing 15 to 30 per cent. of chromic oxide and 30 to 65 per cent. of silica.[1]

Lynam and Rees [2] have found that some chrome-silica bricks to which up to 7·5 per cent. of finely ground silica has been added[3] are stronger than chrome bricks at high temperatures and have a smaller temporary expansion than silica bricks.

The addition of iron oxide makes the bricks liable to crack, though not so seriously as in the case of chrome bricks almost free from silica.

Chrome-silica bricks are cheaper than bricks made wholly of chrome ore or of chrome ore and magnesite. They are less liable to spall than ordinary chromite bricks and silica bricks. They have a smaller thermal expansion (linear) than silica bricks (0·7 per cent. on heating to 1200° C.). The refractoriness under a load of 50 lbs. per square inch is 1450° C.

The best chrome-silica bricks are those in which the bond is composed chiefly of forsterite ($2MgO.SiO_2$), so that it is necessary to have more magnesia present than will form forsterite with all the silica, including that in any serpentine present in the chrome ore.

There appears to be no compound or eutectic of chromic oxide and silica; according to Budnikoff and Mandelgrun,[4] and Bunting,[5] even after heating to 200° C. and cooling the two oxides are immiscible, and the chromic oxide lies enmeshed in a network of tridymite and cristobalite crystals and in an amorphous glass mass. The loss of strength on heating under load is attributed to an increase in the iron compounds in the chromite.

Uses.—Chrome-silica bricks are not sufficiently refractory for use in most open-hearth furnaces, but behave well in other furnaces where the temperature is slightly lower. They are almost neutral in nature, but are more acid than pure chromic oxide on account of the silica present.

CHROME-OLIVINE BRICKS.

Bricks made of chrome ore and olivine are more refractory under load than ordinary chromite bricks. It is advisable to add magnesite so as to produce both chrome spinel and forsterite.

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[1] U.S.A. Pat. 1,814,088 (1932) claims the use of 20 per cent. of finely divided chromite and 80 per cent. of silica rock, with sulphite-lye pitch as a binder.

[2] *Trans. Cer. Soc.*, 1936, **35**, 138–165.

[3] The chrome batch employed contained: chromium oxide, 44·7; silica, 6·8; alumina, 9·5; ferric oxide, 21·5; and magnesia, 16·9 per cent.

[4] *Ber. deut. ker. Ges.*, 1932, **13**, 485.

[5] *J. Res. Amer. Bur. Stand.*, 1930, **5**, (2).

According to Harvey and Birch,[1] a suitable mixture produces bricks containing 50 to 80 per cent. of chromium oxide, 10 to 40 per cent. of olivine, and 4 to 40 per cent. of magnesite.

A mixture of equal parts of olivine and chromic oxide was patented in 1936 (Eng. Pat. 456,207).

IRON-ORE BRICKS.

Several patents have been granted in which the use of iron ore (or " blue billy ") is specified for refractory bricks, but these bricks have only been used to a limited extent. They are made by crushing the ore to powder, mixing it with milk of lime so as to form a very stiff paste, moulding, drying, and burning the bricks in a manner similar to those made of silica.

In E. G. Brewer's patent (1877) the burning temperature is specified as " at red heat or above " ; the proportions of the materials specified in S. Pitt's patent (1882) are 90 parts of ore and 10 parts of slaked lime, with sufficient water to form a stiff paste.

Iron-ore bricks resemble chromite bricks of low grade in most of their properties, but they are much more easily destroyed by reducing conditions in a furnace. Iron ore is a valuable flux for some refractory materials—especially fireclays—but it is seldom a suitable material for the aggregate or chief constituent of firebricks.

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[1] *Brick and Clay Record*, July 1937, p. 42.

CHAPTER VIII.

CARBIDE AND CARBOXIDE BRICKS.

CARBIDE and carboxide bricks are made by uniting particles of carborundum or other silicon carbide or carboxide with a suitable bond, and then forming the mass into bricks which are afterwards dried and burned.

Uses.—Silicon-carbide bricks and slabs are expensive, but they have so high a thermal conductivity that they are being increasingly used in muffles, enamelling furnaces, tunnel-kilns, saggars, kiln-cupboards, and in boiler-settings, regenerators, and other appliances where good heat-conductivity at high temperatures is important. These bricks are resistant to spalling.

Under highly oxidising conditions the carbide decomposes, but it usually does so very slowly, particularly if the bricks are protected with a thin coating of boracic glaze.

Materials.—The chief materials used for these bricks are *carborundum*, *silundum*, *siloxicon*, *carbofrax*, and *fibrox* but other silicon carbides or carboxides may be employed, and some of the foregoing are also used under different trade names. All these substances are prepared by heating a mixture of silica and carbon in an electric furnace, the various products formed depending on the proportions of silica and carbon and on the conditions of heating.

It may sometimes be desirable to use some other refractory substance with the carborundum; thus, in 1903, the Carborundum Co. patented the use of a mixture of equal parts of ganister and carborundum. Siemens & Co., in 1909, patented the use of a mixture of silicon carbide and powdered silicon. W. R. Just, in 1915, patented the use of a mixture of carborundum and zirconia for muffles, crucibles, furnace linings, etc., about equal proportions being recommended. Equal parts of graphite and carborundum, together with 14 per cent. of fireclay as a bond, was patented by H. Wade in 1918.

The following *bonds* have been suggested for the manufacture of carborundum and similar bricks:—

(*a*) *Water-glass* or silicate of soda of specific gravity 1·03 to 1·05 (patented by the Carborundum Co. in 1902) is convenient, but reduces the heat resistance unduly. According to B. Seaboldt, the addition of common salt is advantageous.

(*b*) *Clay* (patented by E. W. Engels in 1902) is good, but causes the bricks to shrink considerably. W. J. Hillis (Amer. Pat., 1916) specifies a mixture of flint 20, plastic clay 10, carborundum 30, and binding clay 40 parts. A. A. Lines, in 1908, patented the use of 4 parts of silicon carbide and 10 parts of clay for gas and electrical fittings such as mantle rings, nozzles, etc. B. Seaboldt, in 1905, patented the use of mixtures of (*a*) siloxicon, clay, and sawdust or chaff, (*b*) siloxicon, clay, sodium silicate, and salt, and (*c*) siloxicon, clay, sodium silicate, salt, and sawdust or chaff with or without the addition of sulphur. T. B. Allen (Amer. Pat., 1916) specifies a mixture of clay, ferric chloride, and carbide. The ferric chloride is decomposed in the burning, and the ferric oxide unites with the clay and forms a very satisfactory bond.

According to M. F. Peters,[1] the clay used, as a binder in carborundum bricks, should have a (*a*) high tensile strength, (*b*) high refractoriness, (*c*) low coefficient of expansion, and (*d*) high thermal conductivity. The proportion of clay required obviously varies with its binding power, but there should be just sufficient clay to cover all the particles of carborundum completely and to form a mass of reasonable strength. This amount is rather less than the percentage of voids in the carborundum.

(*c*) *Borax* or *boric acid* (patented by E. W. Engels in 1902 and A. G. Bloxam in 1905). A. G. Bloxam dissolves the boric acid in glycerin prior to use.

(*d*) *Lime* or *plaster of Paris* (patented by E. W. Engels in 1902).

(*e*) *Portland cement* (patented by E. R. Stowell); about 15 per cent. is used.

(*f*) *Aluminium sulphate* (patented by E. W. Engels in 1902).

(*g*) *Magnesite* or *dolomite* (patented by W. W. and J. S. Hollings in 1902).

(*h*) *Ammonia* (patented by B. Schwerin in 1911).

(*i*) *Zirconium and aluminium silicates* (patented by M. L. Hartmann; U.S. Pat. 1,376,091).

(*j*) *Silicic acid* mixed with a little lime or clay (Eng. Pat. 259,805—1925).

(*k*) *Kaolin and felspar* (Eng. Pat. 284,732—1927).

(*l*) *Spinel* or mixtures or compounds of magnesia, alumina, silica, and lime (Eng. Pat. 419,214—1932).

(*m*) A mixture of silicon carbide, graphite, a flux (clay, borax, or a sulphide), and an organic binder (tar or molasses) (Eng. Pat. 176,436—1920).

(*n*) *Temporary bonds*, such as *glue* (patented in 1900 by F. A. Fitzgerald), heavy *mineral oil*, *tar*, *molasses*, *resin* or *glycerin* (patented by A. G. Bloxam in 1905).

J. B. A. Steurs has suggested a mixture of potassium sulphate 34 parts, sodium sulphite 24 parts, and resin 22 parts, dissolved in alcohol as a bond; the object of using salts in this mixture is not clear.

B. Schwerin (Eng. Pat. 14,285, 1912) claims to have discovered that carborundum (or corundum) when suitably ground and suspended in water, if necessary by the addition of an electrolyte, the water being then separated by electro-osmosis, a plastic mass is formed which requires no other bond and may be shaped in the usual manner. The Carborundum Co., in a patent in 1904, also claim that no bond is necessary if the powdered carborundum is damped, moulded, and heated in an oxidising atmosphere to 1370° C., as the "superficial oxidation unites the particles sufficiently." In another patent granted to the same firm, a temporary bond is used in addition to the heating process. Much emphasis is laid on the self-binding properties of siloxicon by the manufacturers, and it is interesting to note that Gebr. Siemens & Co. in 1910 patented a process in which a similar material (siloxicon carbide) is formed *in situ* by heating carborundum bricks in a current of carbon monoxide.

When no bond, or only a temporary one, is used, the heating must be very prolonged so as to sinter the carbide or carboxide.

The materials should be carefully graded.

Grading.—The size of the grains varies according to the ware it is required to produce. In a patent by the Carborundum Co. (1916), the sizes specified vary between 16- and 100-mesh, suitable proportions of different sizes being mixed together. A mixture suggested in the same specification contains equal parts of 16-, 24-, 36-, and 100-mesh carborundum, a suitable proportion of fine powder being added if desired.

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[1] *Journ. Amer. Cer. Soc.*, 1922, **5**, 181.

An excess of fine material in carborundum bricks is undesirable, but there should be just sufficient to fill the voids between the largest grains, and so produce bricks of low porosity.

Manufacture.—The powdered material and bond are mixed with a little water in a trough mixer or pan-mill, and the stiff paste is moulded by hand, or compressed by machinery (under a pressure up to 3 tons per square inch). The bricks are dried on a warm floor and are burned in a similar kiln to those used for other refractory bricks. It is possible to burn carborundum and similar bricks simultaneously with silica bricks, but this involves a loss, as some of the carborundum is decomposed by the air in the kiln.

Burning.—Owing to the liability of carborundum and similar substances to decompose during the burning, various patents have been granted for the use of special gases to create an inert atmosphere (see Gebr. Siemens & Co.'s patent in 1910 for the use of carbon mon- or di-oxide, and Bloxam's patent in 1905 for the use of nitrogen). In most patent specifications relating to the manufacture of carborundum bricks, the use of an electric furnace is mentioned as being the most suitable. The temperature attained in burning these bricks varies from 1400° C. to approximately 2000° C., according to the particular properties desired. At the lower temperature, the bricks may consist chiefly of silicon carboxide (siloxicon), but above this, decomposition occurs, and at about 1600° C. in a neutral atmosphere carborundum and carbon monoxide gas are formed. According to a patent granted to the Carborundum Co. in 1902, the temperature should be sufficiently high to form a " cellular crystalline structure."

In some cases, the silicon carbide is not produced until the goods are burned. Thus, D. B. Williams and J. R. Stauffer, in 1904, patented the process of embedding the clay articles in ground coke and heating to a high temperature so that silicon carbide is formed.

The British Thomson-Houston Co., in 1912, patented a process which consisted in heating a mixture of 2 parts of carbon, 4 parts of silicon, and 4 parts of fireclay with or without 1 part of manganese oxide in an electric furnace, so as to produce a suitable carbide, whilst Siemens & Co. (1912) heated articles made from a mixture of free silicon and carbon bonded with paraffin or resin to a temperature of 1400° C. to 1500° C. in an oxidising atmosphere, and then to 1600° C. to 1700° C. in an atmosphere of carbon monoxide to secure the formation of carborundum. The British Thomson-Houston Co., in 1913, patented the use of a mixture of silicon in the presence of a catalyst such as fluorspar, pumice, etc., and in contact with gases containing carbon monoxide, dioxide, or both. In a patent by Mineral Products Co. (1915), a mixture of aluminium dust, alumina, calcined alunite, and coke (in the form of finely divided coke) is used, the articles being heated slowly to a temperature of 1500° C. to 2200° C.

On the whole, better results are obtained by using properly prepared carborundum rather than from attempting to produce it indirectly as described above.

Properties.—Bricks made of silicon carboxide (siloxicon), and not heated sufficiently during manufacture to destroy this compound, have a specific gravity of 2·73 and a great resistance to most acids, bases, and alkalies ; they are, however, attacked by hydrofluoric acid, though slowly. The material which affects both siloxicon and carborundum bricks the most severely is lead peroxide, but litharge and lead chromate also have a marked action at a bright red heat. Silica and molten iron separately have little or no effect on the bricks, but, when both silica and iron are present, the bricks are attacked. Slag has a more corrosive action under oxidising conditions than under reducing ones. On prolonged heating at 1600° C., the carboxide is converted into carbide (carborundum).

The chemical composition of carborundum bricks generally shows 77 to 90 per cent. of silicon carbide, 6 to 18 per cent. of silica, and 4 to 5 per cent. of alumina and iron oxide.

Carborundum bricks have usually great mechanical strength—figures as high as 9650 lbs. per square inch having been reached in some cases, and 5700 lbs. per square inch are not uncommon. Unfortunately, the strength rapidly diminishes in use owing to the decomposition of the carborundum when heated in contact with air, but if the bricks have been heated sufficiently to form an impervious skin of silica on the exposed portions, their load-carrying capacity will remain for a long time at 8 to 10 times that of fireclay and sagger mixtures used at the same temperature. Consequently, bricks, plates, crucibles, etc., made of carborundum can be thinner than those made of other refractory materials. Carborundum has the further advantage of not softening in the slightest at 1350° C. as do fireclays. V. Bodin found that the mechanical strength of carborundum bricks decreased up to 750° C., increased up to 1100° C., and then decreased rapidly (fig. 110).

The tensile strength of carborundum bricks is, according to M. F. Peters,[1] proportional to the binding power of the clay, whilst the compressive strength varies as the second power of the percentage of carborundum present. These figures are of general application, but do not always apply to individual bricks, as other factors, such as the size of the particles, also influence the strength.

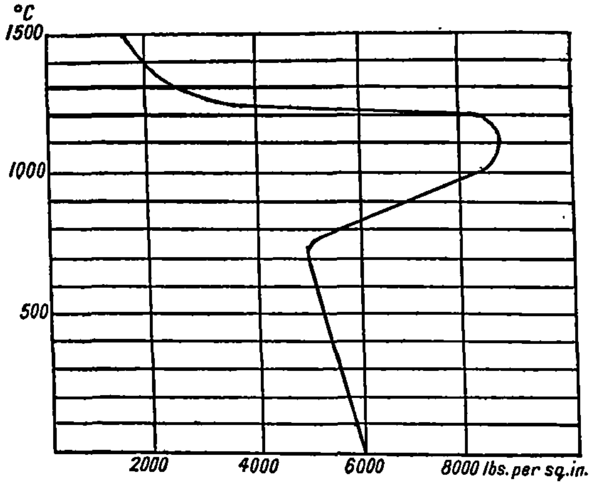

FIG. 110.—Strength of carborundum mixture (V. Bodin).

Articles made of fused (recrystallised) carbide have a high refractoriness-under-load (1500° C.), but contain large pores and are susceptible to excessive oxidation at 900° to 1400° C. Those made of bonded carbide can be made completely impermeable or of any desired permeability.

Carborundum bricks are extremely resistant to abrasion and spalling. Tests of good carborundum bricks made with a fireclay bond showed, after

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[1] *Journ. Amer. Cer. Soc.*, 1922, 5, 181.

heating and cooling ten times, only 0·3 to 8·0 per cent. loss in weight from spalling and less than 0·3 per cent. loss by abrasion.

Carborundum bricks have a very high density and an extremely low coefficient of expansion, viz. 5×10^{-6} up to 1400° C.[1]

Carborundum bricks are exceedingly hard—the sharper fragments will readily cut glass—and their resistance to high temperatures is, for a short time, greater than firebricks made of fireclay, silica, or magnesia. On prolonged heating at 1220° C., however, the carborundum decomposes and the carbon in it gradually burns away without the material being fused. The rate of decomposition is less if the material has first been heated to such a temperature as will effect the fusion of some of the superficial silica, which then provides a glassy coating and largely prevents further oxidation.

The *thermal conductivity* of carborundum bricks is very high, and even when 20 per cent. of clay is present they conduct three times as much heat as magnesia bricks, seven times as much as fireclay bricks, and twelve times as much as silica bricks. Hence, when used in furnace linings, the chief drawback to the use of carbide and carboxide bricks is the facility with which heat escapes through them. For retorts, crucibles, muffles, etc., the high thermal conductivity of carborundum is very useful. For this reason, it is used in the combustion chambers of Dressler ovens.

The thermal conductivity increases with the purity of the carbide and diminishes with an increase in the clay-content. The use of caustic magnesia as a bond gives a higher conductivity than that of clay-bonded bricks.[2]

The *electrical resistivity* of carborundum bricks is fairly low, so that they may be used for lining electric furnaces. According to Hartmann, Sullivan, and Allen,[3] it is as follows :—

TABLE LXXXVI.—ELECTRICAL RESISTIVITY OF CARBORUNDUM BRICKS.

	Resistivity in ohms per Centimetre Cube.		
	Carbofrax.		Refrax.
	A.	B.	
Cold.	Less than 127,000,000	107,200	106·9
800° C.	„ 835,000	12,550	6·45
900° C.	„ 477,000	8,220	3·75
1000° C.	„ 197,000	7,420	4·11
1100° C.	„ 75,000	6,320	3·11
1200° C.	„ 29,500	4,160	2·45
1300° C.	„ 15,200	2,420	2·05
1400° C.	„ 10,100	1,435	1·74
1500° C.	„ 8,590	745	1·62

For other properties of carbides and carboxides see pp. 192 to 197.

Firebricks of clay or other materials may be coated with a carborundum mixture. Engels, in 1899, recommended the use of a mixture of 3 parts of fine carborundum to 1 part of water-glass, painted on to the firebricks to a

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[1] For further information on the thermal expansion of silicon carbide see Rigby and Green, *Trans. Cer. Soc.*, 1938, **37**, 390.

[2] F. Holler, *Wärme*, 1937, (6), 245–251.

[3] *Trans. Amer. Electrochem. Soc.*, 1920, **38**, 279.

thickness of 0·02 inch. A more durable mixture consists of 6 parts of carborundum and 1 part of fireclay. P. M. Grempe[1] suggests that a coating of 70 per cent. of carborundum and 25 per cent. of water-glass will render a second-grade refractory firebrick much more refractory. Where firebricks are particularly basic, 85 per cent. of carborundum may be employed. The coating should be dried for about 24 hours, after which it may be carefully heated until an adherent glassy coating is formed, this latter being extremely insensitive to sudden changes of temperature. Carborundum coatings only 0·02 inch thick are stated to have been found quite satisfactory for lining producers.

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[1] *British Clayworker*, August 1920, p. 113.

CHAPTER IX.

REFRACTORY BLOCKS, SLABS, AND HOLLOW WARE.

BLOCKS AND SLABS.

BLOCKS made of refractory materials are of various shapes and sizes, and are used for many different purposes.

Uses.—Rectangular blocks are chiefly used instead of a corresponding quantity of firebricks, either because the use of firebricks is inconvenient or is less satisfactory, or where the shape required is best fitted by a single block instead of several bricks and where it is desired to have as few joints as possible on account of the corrosive action of slags, frits, glass, etc.

Arch-blocks are used to form parts of arches; they are superior to bricks for the construction of springers and for those parts of arches which require to be perforated. Blocks are also used to form the keystones of arches.

Blocks of special shapes are used for filling acid towers, stoves, regenerators, recuperators, etc., and in the construction of coke ovens, furnaces, etc. In some instances, these blocks require to be specially resistant to acids; in others they must be highly resistant to slags, metallic oxides, glass, or the destructive action of flame and reducing gases.

Hollow blocks are used for flues, gas-burners, recuperators, etc., and where lightness is important. They are often more refractory than solid ones.

Blocks used for constructing *tanks in glass furnaces* are exceedingly difficult to make, as they are subjected to such severe treatment when in use. They must be able to withstand the action of the molten glass and of the materials used in its manufacture; they must resist abrasion and must not discolour any glass melted in them. For this purpose, they must be made of a moderately fine grog and a plastic clay, with the precautions mentioned in Chapter XIII. in connection with glass pots.

Blocks are made as large as 3 feet by 2 feet 6 inches by 2 feet, but the risks in manufacturing such large sizes are so great that preference is given to blocks measuring 2 feet by 2 feet by 2 feet or less.[1]

Slabs or "quarries" are made of various sizes up to 40 inches by 24 inches by 4 inches, though few firms regularly supply them measuring more than 24 inches by 24 inches by 3 inches. These slabs are used for building "cupboards" in kilns, paving the floors of furnaces and slip kilns, lining enamel kilns, the tops and sides of flues, and for a variety of other purposes. Some slabs have a rebate at each end so that a gas-tight joint may be made, or for the better support of neighbouring slabs.

Materials.—The materials used for making blocks and slabs are the same as those used for bricks employed under the same conditions, and they are prepared in a similar manner. The chief differences are: (*a*) the use of larger

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[1] See footnotes on pp. 515 and 547.

pieces of grog in addition to the sizes used for bricks; (*b*) in the case of clay blocks, the use of a stiffer paste which has been allowed to sour, and has been passed several times through a mixer; and (*c*) slower drying and burning.

The coarseness of the grog should be regulated, according to the size of the blocks, as, unless large blocks are made more porous than small ones, it is difficult to dry and burn them completely. For small blocks, the grog should pass through a screen with $\frac{1}{8}$-inch holes, but be retained on a screen with $\frac{1}{32}$-inch holes. For large blocks, about one quarter of the grog may pass through a screen with $\frac{1}{4}$-inch holes, and be retained on one with $\frac{1}{8}$-inch holes; one half may pass through a screen with $\frac{1}{8}$-inch holes, and be retained on one with $\frac{1}{16}$-inch holes, and the remainder of the grog should pass through a screen with $\frac{1}{16}$-inch holes, but be retained on one with $\frac{1}{32}$-inch holes. The proportions of grog of these various sizes should, however, be varied to suit the purposes for which the blocks are to be used; thus, blocks to be used in tanks for melting glass require to be specially resistant to corrosion, and, therefore, must have a closer texture than blocks which are merely required to resist high temperatures, and so may have a coarser and more porous texture.

As a general rule, when refractoriness is the chief requirement, the grog may consist largely of particles of one size, but, when resistance to corrosion is important, three sizes of grog should be used in such proportions that the particles of the second size fill, as much as possible, the voids or interstices between the largest pieces of grog, whilst the amount of the smallest sized grog should be such as to fill, as far as possible, any voids left in the mixture of the two larger sizes. The proportion of clay should be sufficient to coat each piece of grog with a thin film, and afterwards fill any remaining voids. This method of proportioning the grog and clay will give a block of maximum density; it will be too dense for many purposes, in which case the pieces of grog should be as much more uniform in size as the case demands.

The clay for blocks should be finely ground and should pass completely through a 30-mesh screen; it is still better if it can be washed completely through an 80-mesh screen, as much material between 0·033 and 0·005 inch diameter is not desirable in refractory blocks.

The grog and clay should be weighed in the desired proportions, and mixed in a dry state in a blending machine, or in a double-shafted trough mixer, prior to adding any water. The mixture should then be passed into a trough mixer (fig. 43), where the necessary proportion of water (which should never exceed 25 per cent., and more usually is only about 10 per cent.) is added, and incorporated, after which the mixture should be pugged, and cut off in blocks, about 12 inches by 9 inches by 6 inches, and set aside to "sour." During the souring the blocks must be kept moist externally, by covering them with wet sacking, which is wetted daily, and no dry crusts must be allowed to form. After about a month's storage the blocks should be re-pugged, and again set aside, under the same conditions as before, this process of storing and pugging being repeated as often as may be considered desirable. In blocks having to resist high temperatures and corrosion for long periods, *e.g.* those used in tanks for melting glass, three or four months' storage is by no means too long, though it is not usual to store the clay for more than three or four weeks. The longer storage is, however, of greater benefit.

The majority of clays used for the manufacture of very large articles of the fireclay class contain upwards of 65 per cent. of silica, about 30 per cent. of alumina, about 1·5 per cent. of iron compounds, and the same proportion of fluxes.

Clay for large articles should not be too fine or it will not withstand repeated changes of temperature so easily as a coarser clay. It is in consequence of this that grog, whose particles are much larger, is greatly used for the production of large ware. The larger the blocks, the coarser must be the grog used in their manufacture, as large blocks require to be more porous than smaller ones on account of the difficulty of drying their interior.

For large slabs, 4- to 20-mesh should be used up to about 50 per cent. Even a small proportion of fine grog has an adverse effect except where the articles are subject only to compression; fine grog may then be used with advantage.

If a paste is used it should be as stiff as can be worked satisfactorily, because the larger the proportion of water, the greater the shrinkage on drying and the more risk is there of the blocks being cracked or twisted. Where the material is to be rammed into the mould (fig. 107) it should not be so moist as a paste, but should be of the consistency of freshly dug loam.

Souring is particularly necessary in the case of a clayey material to be used for blocks, as a uniform distribution of the moisture can only be effected by this treatment, and any irregularity in this respect is a frequent cause of cracks and other defects. Unless the paste used for making blocks is kept for a sufficiently long time—for some purposes three months is not too long—the resulting blocks will not possess the maximum resistance to changes in temperature and to corrosion.

Making.—Slabs and blocks are made by hand-moulding in a manner similar to firebricks. It is generally recognised that very large *clay blocks* are most conveniently made in moulds. The principal difficulty with regard to using moulds of the ordinary box type for large blocks is that the latter are very liable to be distorted when turning them out of the mould, and also that very large box-moulds have a smaller output than moulds with loose sides, as the former require several men whilst the latter can readily be filled and emptied by one man. Much better results are obtained by employing wooden moulds without a bottom for slabs, whilst for thicker blocks the wooden mould should have loose sides held together by nuts and bolts or by hooks and eyes, so that the sides can be removed without disturbing the contents when the latter is complete. When designing loose-sided moulds for the preparation of large blocks, it is desirable to taper the sides slightly so as to allow ⅛ to ¼ inch extra shrinkage at the bottom of the mould on account of the paste behaving somewhat like a fluid and "settling" during the drying.

The moulds may be made (i) throughout of wood, *e.g.* exterior hardwood fitted with a softwood lining, (ii) of wood and lined with plaster of Paris, (iii) throughout of plaster, reinforced with ¼-inch iron rods, or (iv) of wood with either a loose lining of wet calico or a more permanent lining made of calico wetted and tightly stretched on the insides of the mould.

When a mould is made wholly of wood, the inner surface may be lubricated to facilitate removal without the clay sticking to it. The lubricant may be (*a*) paraffin or crude vegetable or mineral oil, but this has several disadvantages, and is liable to cause cracks due to the carbonisation of the oil during firing. It also tends to cause flashed goods, so that oil-moulded bricks are usually distinguishable by their colour. These difficulties may be to some extent avoided by the use of lard oil, or any other oil which is volatilised at a low temperature; (*b*) sand, as in sand-faced bricks, but this practice is unhealthy for the workers and should be avoided—fine hardwood sawdust is equally efficient in many instances and is less unhealthy; (*c*) water, which is usually of very small value as a lubricant for very large moulds.

Instead of the mould being filled at one "throw," small masses of paste are thrown with great force into it and are then tamped or beaten until every part of the mould is completely filled with a compact mass.

It is important to fill the corners first and gradually to work towards the centre, as, if this is not done, the corners and arrises of the block will be imperfect or weak. This precaution is particularly necessary for blocks with many projections, such as Cowper blocks (fig. 111), patented by E. A. and C. E. Cowper in 1882.

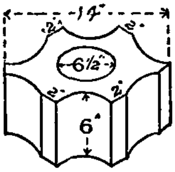


FIG. 111.—Cowper block.

In some cases, when hand-moulding large blocks, a large lump of clay paste is placed on the bench and wedged and worked until free from air-bubbles. It is then lifted and thrown forcibly into the mould (the latter being on the floor) with the help of an assistant if the clay is too heavy to be lifted by one man. The mould is then lifted by the moulder and his assistant and dropped on the floor four to eight times. This strenuous procedure usually ensures the clay filling the mould uniformly. Any surplus paste should be removed with a wire or strike, and the surface thus exposed may be smoothed, if desired, by means of a palette knife, scraper, or rubber. It is a mistake to remove the surplus clay with too wet a strike, though this is often done to make it easier for the workman and to save time. The wet wood forms a soft, sloppy surface, which shrinks at a different rate and causes superficial cracks on the slab.

The leaner the paste, the more necessary it is to tamp it vigorously in order to consolidate it, and, if the block is very large, it may be necessary to fill the mould in a series of layers and to beat each into position before adding the next (fig. 107) or even to tread the paste down with the feet.

If the block is large, the mould may next be lifted by means of a pulley block and chains, or it may be taken to pieces, and so removed, leaving the block either on the base-board or on the drying floor.

It will improve the blocks if they can be made on a slab of paste of the same composition, such as would be produced by laying the mould on a plain frame about ¾ inch thick and passing a taut cutting wire between this frame and the mould after filling the latter. Alternately, it may be preferable to invert the mould with its contents on a slab of paste similar to that used for making the block, or on a bed of sand or fine grog. If the blocks are laid on a board or the floor, they cannot "creep" properly when shrinking and are much more liable to crack than when laid on a clay slab or on sand. Moreover, boards are liable to warp, and so form misshapen blocks.

Great care must be taken in removing the sides so as to avoid spoiling the surface of the articles.

The surfaces of the blocks are smoothed with a palette knife, scraper, leather, or rubber.

It is unwise to commence making a block so near to "closing time" that it cannot be finished. To leave an unfinished block is often to court disaster, even when it is kept covered with wet cloths.

Some blocks are made by beating a large mass of material into a block of indefinite shape and allowing this to stiffen slightly. The block is then cut or carved to the shape required, as though it were made of soft stone.

Solid blocks are sometimes made by expression from a machine and are cut into suitable lengths with wires, but the softness of the paste required for such a process of manufacture is not in favour of its use for refractory goods, for the reason mentioned on p. 278.

Solid blocks of special shape may be made by cutting a plain block to the desired shape, usually with the aid of a template or of a device such as that shown in fig. 47.

Cowper blocks, and some others, when made in a die-press, are shaped more accurately, cheaply, and better than by hand, and are more readily sold than hand-made blocks, especially those for arches. At the same time, it is often as cheap and equally satisfactory to make these Cowper blocks with an ordinary pug mill and mouthpiece, or in a pipe-press similar to those used for glazed drain-pipes, and then to cut them to the correct height with a wire cutter. Special care is required in drying these blocks, as variations in the size and shape are particularly objectionable. These variations can be largely overcome by allowing the clay band to run over a well-oiled set of rollers, both before and after cutting, and permitting the blocks to dry slowly and regularly, particularly at first. They are turned when half dry ("leather-hard"), so as to secure their being regular in shape.

Tamping is often preferred to filling the mould with soft paste when large blocks are required. In this method, a little of the material having the consistency of freshly dug soil is placed in the mould and consolidated by repeated blows from an iron-shod tamping tool, or preferably a pneumatic hammer (fig. 107), which ensures more regular blows and is less tiring to use. A further quantity of material is then added, tamped as before, and the process is continued until the mould is quite full of tightly rammed material. To ensure success, certain precautions should be taken, the most important ones being (*a*) to have a mould of sufficient strength, as the pressure exerted during the tamping is very great; (*b*) to have the interior of the mould well lubricated with a mixture of paraffin and either rape or linseed oil, and then "sanded," or dusted with fine grog or sawdust; (*c*) the man in charge of the tamping should begin at the sides of the mould and work gradually to the middle. He should pay special attention to the corners, as these are usually the most difficult to fill properly; (*d*) before adding fresh material to that which has already been tamped, the surface of the latter should be roughened with an iron comb or a piece of saw blade, so as to secure as intimate a contact as possible between the old and new material; (*e*) it is scarcely possible to tamp the material too much, but there is always a risk of not tamping sufficiently; (*f*) the after-filling of the mould, with all its drawbacks, may be avoided by placing a wooden collar about 4 inches high around the top of the mould, and filling the mould almost to the top of the collar, so that when the material has been sufficiently tamped, the mould is just filled and the collar may be removed.

Notwithstanding the greatest care, some blocks will split during the drying and the burning at parts where fresh paste was added in the moulding. This defect is more noticeable if the workman stands at the same height throughout the tamping process, because at the beginning he is "well above his work" and tamps sufficiently, whilst in the later stages he may be rather too low and his blows are less powerful, so that blocks which have been tamped with a pneumatic hammer, or other mechanical device, are often sounder than those which have been tamped by hand.

Pressed Blocks.—All kinds of blocks may be made in powerful presses (figs. 51–53), but, generally speaking, they are more sensitive to sudden changes in temperature than blocks made by hand, or by the use of a hand-operated press instead of a power-driven one. This may be overcome by particularly careful grading, and by the use of presses of ample power with both top and bottom pressure. A press which has proved particularly useful for large boiler and other blocks up to 36 inches by 24 inches by 18 inches, and can also be used for saggers, is made by the Brightside Foundry & Engineering Co., Ltd.

The control is quite simple, only one hand-lever being required for starting, stopping, and reversing the press.

The pressing of large blocks has not been studied as fully as is desirable, and the failures of power-pressed blocks in the past may merely indicate that the necessary conditions for success have not been found. The great improvements recently made suggest that power-pressed blocks may be used extensively in the future, as their great accuracy of shape enables much closer joints to be made than with hand-moulded blocks.

Casting from slips is being increasingly used (see p. 664).

Electro-cast blocks are made by fusing the material in an electric furnace, pouring the molten mass into iron or sand moulds and cooling slowly.

Fireclay blocks are made in wooden moulds or by "building up" and "modelling."

Sillimanite blocks are made in wooden moulds or by slip-casting.

Silica blocks are usually made in wooden moulds by the process of "tamping" described on p. 542. They are very friable when freshly moulded, and require exceptional care in removing them from the mould, especially if, as is often the case, it is necessary to tap the latter so as to loosen adherent portions of the block. Air entangled in the interior of the blocks occasionally causes small pimples on the surface. These may be pricked with a needle. The surface of the blocks may be smoothed with a scraper followed by a leather or rubber.

Carbon blocks are made like bricks of the same material, in wooden moulds. These must be strongly made and so constructed that they can be taken to pieces, leaving the block in position.

The so-called *graphite slabs* used for flattening window glass require special care in manufacture, as they must not be sensitive to sudden changes in temperature and must have great mechanical strength. They are satisfactorily made from a coarse-grained mixture, but the surface (which is polished) is made of a finer material. Well-known recipes for these slabs are—

	A.	B.
Fireclay	2	1 parts.
Grog	2	1 ,,
Graphite	1	2 ,,

The materials are mixed in the dry state and the mixture is passed through a No. 10 sieve, a portion being passed through a No. 25 sieve so as to form a fine surface. The mixture is made into a stiff paste by pugging, and this paste is then allowed to sour for a few days, after which it is either pugged or trodden, the souring and mixing being repeated on alternate days for about a fortnight. The slabs are moulded in a wooden frame in a similar manner to bricks, the final surface being made with the finer clay. Usually, it is convenient to place this finer clay at the bottom of the mould and to fill it with the coarser material.

The burned slabs are sorted carefully and the sound ones are polished with wet sand, followed by finely ground grog, and, finally, with pumice stone or talc, the friction being applied by a sandstone block held in a double-handled frame.

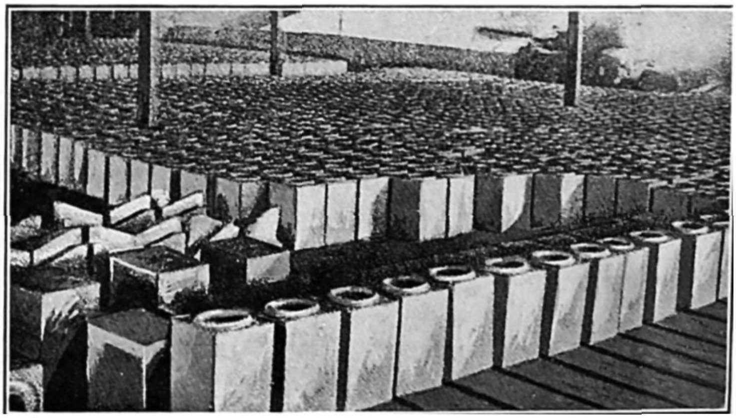
Magnesia blocks are made in the same manner as magnesia bricks. They are difficult to make and are seldom used.

Lime blocks for electric furnaces, etc., must be cut out of lumps of quicklime; they cannot be moulded satisfactorily.

Drying.—Special care is needed in drying large blocks. They are usually dried on the floor of the building in which they are made. This floor may be provided with steam-heated flues, so that its temperature may be gradually increased as the blocks dry. A less satisfactory alternative is to have only a part of the floor which can be heated and to move the blocks on to this part when they are able to bear the heat.

It is often convenient to arrange racks upon which the goods may be placed, the highest racks being used first and the goods moved gradually downwards nearer to the hot floor as the drying proceeds. For blocks of large size, the use of racks is impracticable, and even for those of medium size there is often a danger that the racks will twist or warp and so produce misshapen blocks. Some firms prefer a false floor or a wooden grid (fig. 112).

A tunnel dryer (with cars) in which the humidity and temperature can both be accurately regulated, is the best type of dryer for all but the largest blocks.



(Photo by K. Seaver.)

Fig. 112.—Typical section of hot floor, showing coke oven silica bricks (" gun " shapes) in process of drying.

It is not wise to dry large blocks on the top of a kiln, for the temperature thereon is too irregular to give satisfactory results.

When possible, the blocks should be turned on edge during drying, so that each side may, in turn, be exposed to the air.

The blocks should be handled as little as possible during the drying, as they are very friable and easily damaged. When dry, they should be taken to the kiln, as they soon spoil when exposed to moist air.

One of the most essential features of successful drying consists in a steady, gradual rise of temperature at a sufficiently low rate, and, in the case of large blocks, this necessarily means a large amount of space, well sheltered from draughts by a number of temporary partitions surrounding the goods and so arranged that various compartments may be heated to different temperatures

The drying must not be unduly hurried; in fact, speed must be sacrifice to safety when a floor is used. Hollow blocks and those of small size ma be dried with moderate rapidity, but larger blocks may require several weeks or even months, before they are completely dry. This time cannot be safel reduced when the customary methods of drying are used, but the author has done so by placing the blocks in a small temporary tunnel or closed stove and heating them with saturated air (so that the temperature is raised without the blocks drying), and afterwards allowing the evaporated water to escape, whilst maintaining the goods at a high temperature. This treatment converts all the moisture in the goods into vapour without allowing the exterior to harden and, in this way, prevents cracking.

In any case, the course of the drying must be constantly watched, the air-supply carefully regulated, and the ventilation effected in such a manner that there are no local air-currents of a nature likely to injure the goods. The Buckeye Clay Pot Co., Toledo, Ohio, claims to have secured exceptionally good drying by building the walls of a tunnel dryer of very porous bricks and the top of plaster slabs. In the tunnel, blocks for glass-melting tanks remain for three weeks.

It is specially important that no portion of the outside of the block should become quite dry so long as the inside is still moist, and covers must be used for portions likely to dry too rapidly, or the articles must be heated in an atmosphere saturated with steam, as described above.

It is worth while occasionally to break or saw a dry block into two pieces so as to see whether it is thoroughly dried. This apparent sacrifice is well worth its cost, and the latter may be reduced by selecting a block, the two halves of which can be sold separately.

Failure to dry blocks in a proper manner is the chief cause of cracks, though the use of too wet a paste is also a frequent cause of this defect. Cracks in blocks which are not quite dry may be repaired by scratching both sides of the cracks, so as to make a wider opening. This opening is then well wetted with a damp cloth ; some stiff clay is rammed in and, as it dries, the surface of the block is again made smooth. If the work is properly done, the block may be as sound as any other, and will be as good in quality as if the crack had never appeared.

Although uniform drying is essential, it is neither necessary nor desirable that the blocks should be absolutely bone-dry before taking them to the kiln. " Over-dried " blocks are very friable and difficult to handle, whilst blocks which still contain 5 per cent. of moisture (though they appear to be " white hard ") are much easier to move and are far less liable to be chipped. The final 5 per cent. or so of moisture is easily removed in the first stage of burning without any risk to the goods.

Finishing.—During or after the completion of the drying, the blocks should be examined and finished with a knife and rubber. In some American works, blocks of special sizes are sawn from larger (fired) ones by means of a 5-foot carborundum toothed saw, which cuts rapidly and leaves the blocks with a very smooth surface.

Taking to Kiln.—The transport of large blocks to the kiln requires special care. All shocks must be avoided by the use of resilient bedding (sacking, etc.), and of cars or trolleys with good springs. Where blocks are sufficiently light for one or two men to carry them, the use of a stretcher or " hand-barrow " is often more satisfactory than the use of cars or trolleys.

Kilns.—Blocks may be burned in almost any kind of kiln suitable for firebricks, though preference is usually given to single round down-draught kilns. This is due to the fact that these kilns have been used ever since refractory blocks were first made, rather than to their superiority over any other type of kiln for this purpose. Continuous chamber kilns, if suitably designed, give equally satisfactory results and require less than half the fuel.

Setting.—Blocks are usually stacked one above the other in rows or rings, a small space being left all round each block for the kiln gases to circulate uniformly. Blocks of irregular shape must be arranged as uniformly as circumstances permit.

Slabs are usually set in a vertical position, as they then twist less than when they are laid flat in the kiln.

Moderately large blocks are preferably set near the top of the kiln so that they are less likely to be subjected to any strains during the firing, but much depends on the goods supporting them. When rectangular kilns are used, it is a very good plan to make a floor of burned bricks on which the largest blocks and specially shaped articles may be placed, because the more nearly the whole of the block is supported, the less liable it is to distortion or cracks or to become discoloured. Finely powdered sand has been used in setting large shapes, but as there is some risk of inhaling it, the new Government regulations should be carefully followed. Slabs or cubes of very stiff clay-paste usually make an excellent bedding material.

Where it is necessary to protect the surfaces of large articles from direct contact with the flames, etc., they should be surrounded by slabs or by cheaper ware.

It is important that the blocks should be well bedded, steady, and solid, or they will twist and crack during the burning.

Burning.—Blocks are burned in the same manner as bricks, but the temperature during the burning must rise very steadily, or the blocks will be cracked. Refractory materials are necessarily poor conductors of heat and, consequently, the outside of the block may be at a red heat whilst the interior is nearly cold. If this wide difference in temperature occurs, the internal strains produced thereby will usually result in the formation of cracks, whereas with a slower rise in temperature the heat will be distributed more uniformly throughout the blocks, and cracking will be avoided.

The critical temperatures in burning blocks are: (*a*) below 600° C., when the clay is being dried and decomposed, with the evolution of much steam; if the blocks are heated too rapidly at this stage they will certainly crack. The large amount of water-vapour ("steam") set free when clay is first heated in the kiln is often overlooked and so causes difficulty. It is not usually realised that at least 1½ cwts. of water is given off from each ton of clay in the kiln and, consequently, the arrangements for the escape of this large amount of steam (about 5000 cubic feet per ton of clay) are neglected.

(*b*) At a temperature of 900° C. to 950° C., when any carbonaceous matter is being burned off and the tendency to form black cores is at a maximum. This stage of burning must not be hurried, or the blocks will show cores when broken. The exact length of time required can only be learned by experience, as it varies with each size and shape of block, as well as with the size and number of pores in the mixture.

Towards the end of the burning, it is particularly necessary to heat slowly and to maintain the temperature for a considerable time, for prolonged heating at a lower temperature effects the same changes as a shorter heating at a higher temperature, but with less risk of damage.

(*c*) The final "soaking," during which the fusible bond which unites the other particles firmly together is formed. This should not usually be less than forty-eight hours, when the blocks are required to resist corrosion, and may require to be much longer if the blocks are very large and close in texture. There is often a tendency to shorten this "soaking" time unduly, with the result that weak blocks are produced.

The finishing temperature of the kiln must depend on the purposes for which the blocks are to be used.[1] The rule given in previous chapters—to burn the goods at a higher temperature than they are likely to reach in use—applies equally to blocks of all sizes and shapes. Unless this is done, the blocks may cause trouble by shrinking when they are used. If this shrinkage is unimportant, the manufacturer may effect a considerable saving by burning the blocks at a temperature equivalent to Seger Cone 5, which will give sufficient strength for the blocks to withstand all shocks of ordinary transport, handling, and use. Unfortunately, a high rate of shrinkage is often accompanied by a severe warping or twisting of the blocks or slabs.

A. Reynolds has patented (111,355, 1916) a method of increasing the resistance of fireclay articles such as nozzles, stoppers, etc., to heat and corrosion, which consists in embedding them in the floor of a furnace and subjecting their surface to a temperature sufficient to produce incipient fusion. This gives the surface a hard, dense structure which is very resistant to the action of molten metals and slags.

Cooling.—The kiln must be cooled very slowly, so as to anneal the blocks without cracking them. Just as the rise in temperature must be slow in burning large ware, so must the cooling. If the temperature of the kiln is lowered too rapidly (especially between 1000° C. and 50° C.), it will be a fruitful source of dunted and cracked ware, and though considerations of cost must tend to prevent the goods remaining too long in the kiln, every endeavour should be made to bring about the cooling as steadily and slowly as possible.

Properties of Blocks.—The chief properties required of refractory blocks are accuracy of shape, refractoriness, strength, and durability, but several other properties are sometimes of importance.[2]

Accuracy of Shape.—It is extremely important that blocks of special shape or size[3] should be accurately made. The greatest permissible variations are often as low as 2 per cent., and with a material like clay or silica it is by no means easy to work within so narrow a limit. This accuracy can only be secured by keeping the proportions of the various materials as uniform as possible, and particularly by avoiding an excess of water and irregular burning.

Where great accuracy of shape is desired, some manufacturers make the blocks rather larger than the size ordered and grind the burned blocks accurately to shape and size on a carborundum wheel. When this is done, care should be taken not to grind any face of the block which is likely to be exposed to flue-dust, slags, etc.

In this connection it is important to note that refractory blocks are frequently sold by weight, and when a quotation is made for a block of unusual shape or pattern, its weight must be calculated from the drawings. To guess at the weight of the burned goods is clumsy and often inaccurate. The best method of calculating the weight is to ascertain by actual trial the exact weight of 1 cubic foot of the burned material; this will depend on the proportion of grog, clay, silica, etc., in it. The volume of the block or other article must then be found by the ordinary methods of mensuration, and this volume (in cubic feet), multiplied by the weight of 1 cubic foot of the burned clay, will give the weight of the article when burned. When the shape of the article is highly complex, the calculation may often be simplified by imagining it

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[1] Glass-tank blocks should be burned at Seger Cone 12 to 14 (about 1350° C. to 1400° C.).

[2] The properties of glass-tank blocks are described in Chapter XIII.

[3] In order that warping, cracking, and irregular shrinkage or expansion may be avoided as far as possible, the sizes of blocks must be kept within reasonable limits. Under ordinary conditions of manufacture, one dimension should not exceed 6 inches, and the greatest dimension should not exceed 3 feet. Slabs more than 30 inches by 30 inches are very difficult to produce if they are less than 3 inches or more than 4½ inches thick.

divided up into a number of simpler forms, and adding the volumes of these together.

Refractoriness.—The resistance of a block to heat will depend largely on the materials of which it is made, so that the information on refractoriness given on pp. 364 and 455 will apply to blocks. In any case, blocks must be sufficiently refractory not to twist or warp when in use.

The apparent refractoriness or durability of fireclay blocks may be increased by making them hollow, with very thin walls, and leading a current of air or kiln-gases through them. The author knows several instances where solid blocks have failed to resist the heat in commercial furnaces, but their replacement by thin rectangular slabs of the same material has proved entirely satisfactory.

Changes in Temperature.—All refractory blocks should bear variations in temperature without cracking, spalling, or breaking, and, as far as possible, they should not be damaged if one part of a block is heated or cooled more rapidly than another.

The more open the texture of the ware and the less it is burned, the more quickly is the temperature of the mass equalised, and the less liable will it be to crack or break. In dense blocks which are partially vitrified, the conductivity is less, it is more difficult to keep the temperature equal, and the result is that the goods expand irregularly, causing unequal tensions, which the mass cannot resist and so breaks or cracks.

Crushing Strength.—The resistance of a block to crushing is seldom specified in an order, though this property is often of extreme importance. If well made, blocks should show a considerably greater crushing strength than bricks of a similar material (*q.v.*). The highest strength and refractoriness cannot be united in one block, as these properties are incompatible. Hence, the user must decide the extent to which he will compromise with regard to them.

Resistance to Slags, etc.—The durability of blocks when exposed to the action of slags and hot gases is similar to that of bricks of corresponding texture and composition. A structure built of blocks will usually last longer than one made of bricks, because there are fewer joints in the former, and it is the joints which usually prove the chief source of weakness. The most resistant blocks are those with the closest texture, provided that this does not make them too sensitive to unavoidable changes in temperature. Where resistance to acids is of great importance, the blocks must be heated until a considerable amount of vitrified material has formed, notwithstanding the fact that this treatment reduces their ultimate refractoriness.

A. Reynolds has patented a method of increasing the durability of large fireclay articles by heating the exposed surfaces of the block to a temperature of incipient fusion so as to form a refractory glaze which will increase the life of the article.

Porosity.—The larger the block and the closer its texture, the greater is the risk of its " dunting " or cracking. Hence, it is desirable that blocks should be as porous as the conditions of use will permit. This porosity should be secured by the use of coarse grog or kieselguhr, and not by the addition of combustible substances such as sawdust.

Shrinkage.—Blocks should not shrink or expand much in use, though a slight shrinkage is almost unavoidable with those made of clay. A large amount of shrinkage indicates that the blocks have not been burned sufficiently.

Blocks made of silica may *expand* in use if they have been insufficiently burned.

REFRACTORY HOLLOW WARE.

Under the term "refractory hollow ware" is included many kinds of articles, such as saggers, muffles, crucibles, scorifiers, glass pots, retorts for the manufacture of coal gas or the distillation of zinc and other metals, outlets and stoppers for furnaces, linings for ladles and a variety of other articles too numerous to mention; the more important of these are described in subsequent chapters.

Refractory hollow ware must be able to withstand high temperatures; it must not be sensitive to such sudden changes in temperature as are unavoidable in its regular use; it must have sufficient mechanical strength and, in the case of crucibles and glass pots, it must not be too readily attacked by metals, metallic oxides, slags, etc.

Most refractory hollow ware is made of a heat-resisting skeleton (as grog), the particles forming which are united by a bond of highly plastic clay.

Hollow blocks may be hand-moulded, the workman inserting a core before filling the mould and afterwards withdrawing it, leaving the hollow space.

Hollow blocks may also be made in an expression machine fitted with a special mouthpiece containing one or more cores. The clay paste is formed by the machine into a hollow column, which is afterwards cut into suitable lengths by means of a cutting table. The process is precisely the same as that used for "wire-cut bricks" (fig. 99), except that the cores within the mouthpiece produce hollow instead of solid goods.

Ladles for receiving molten metal from metallurgical furnaces are usually lined with refractory bricks, which must be able to stand sudden changes of temperature without spalling.

The bricks for lining ladles should be accurate in shape and size, with joints of minimum thickness. The joints are filled by dipping the bricks prior to use. Careful drying before use is essential.

Ladle bricks should also be dense and highly resistant to corrosion and abrasion by the metal and slag. The refractoriness is of secondary importance and need not exceed that of Seger Cones 26 to 28. The bricks should be highly resistant to sudden changes in temperature. The texture should be uniform and the pores very small; a porosity of 16 per cent. (water absorption) is satisfactory, but it is the smallness of the pores rather than their total volume which matters.

Steel manufacturers who use ladles may be divided into two groups:

(*a*) Those who prefer a siliceous lining containing not more than 30 per cent. of alumina.

(*b*) Those who prefer a lining containing more than 30 per cent., preferably more than 40 per cent., of alumina.

At present it is difficult to decide between them as local conditions vary so greatly in different works. There is also a distinct need for a good basic lining for ladles, but none of the basic bricks available appears to be wholly satisfactory, though some users are pleased with basic bricks. Pending the discovery of really reliable basic ladle bricks, the preference, on the whole, appears to be for bricks made of fireclay with a fairly high alumina-content, but which undergo superficial fusion when in use. This prevents slag from entering the lining and so reduces disintegration. To ensure this, a highly refractory fireclay is sometimes mixed with a less refractory clay.

When fluorspar or manganese oxide is present in the slags the ladle linings should contain as little free silica as possible. Aluminous fireclays are also more resistant than silica to slags rich in lime. Bricks with large pores are objectionable, so that the physical properties are sometimes more important than the chemical composition.[1]

Fireclay bricks with 30 to 40 per cent. of alumina are chiefly used, but others are sometimes employed, *e.g.* a mixture of carbon (graphite) and ganister was patented in 1928 (Eng. Pat. 312,700), and, according to A. M. McKendrick,[2] the best ladle bricks are made of plumbago (see "Plumbago Crucibles," p. 586), but no suitable jointing material for them is known, nor has any process been discovered which prevents weak edges due to the flakiness of the material.

For acid steels, ladle linings are best if made of fireclay, preferably with grog. For basic steels a basic lining for the ladles is, theoretically, best, but in practice is not always satisfactory, and fireclay bricks are generally used both for acid and basic steels. It is a curious fact that bricks made by the semi-dry process often make more durable linings than those made by other methods.

Silica bricks are usually too sensitive to sudden changes in temperature, though this is lessened if they are coated with a mixture of fireclay and grog, but in the United States silica bricks are often preferred to those of fireclay.

Magnesia bricks made of fused magnesite are satisfactory, but bricks made of dead-burned (not fused) magnesite are often unreliable in ladles.

Sillimanite bricks have not been used extensively for ladles. Some users claim that they are not sufficiently resistant to the erosion of the metal and slag; but their extraordinary resistance to sudden changes in temperature is shown by the fact that a sillimanite (mullite) brick may be thrown into a steel-melting furnace, raked out at a white heat, and one half of the brick chilled by immersion in water, without serious damage.

Zirconia bricks appear to be too costly, but, otherwise, are satisfactory if made of pure zirconia.

Under-burned bricks are very dangerous to the men using the ladle.

The grading of the material used for the bricks is important, as too porous a mixture is too permeable to slag and too weak to be satisfactory, whilst bricks which are too dense spall readily. The bricks in the ladle may be coated with a tamped material of a refractory nature or with a refractory cement (p. 800). Another good method of coating a brick-lined ladle is to blow pieces of old ladle-lining, previously crushed to pass $\frac{1}{16}$ in. mesh, without any binder, by means of a cement gun using air at 80 lbs. per square inch pressure.

In the United States a tamped mixture of grog 60, fireclay 20, and silica 20 parts is extensively used; this greatly increases the durability of the brick-lining. In most cases, ladles lined completely with tamped material (*i.e.* without any bricks) are not satisfactory.

Ladles should be thoroughly dried before being used, or they will soon be destroyed. The drying may be by a coke fire or oil- or tar-burner beneath the inverted ladle, or by a coke brazier lowered into the ladle.

Fireclay ladles can generally be used for 10–12 basic casts or 25–45 acid casts, but much depends on the nature of the metal and on the length of time the metal remains in the ladle.

For further information on bricks for ladles see p. 781.

Outlets, nozzles, stoppers, sleeves, and *runners* are usually made of fireclay containing 25 to 35 per cent. of alumina and 45 to 60 per cent. of silica mixed with varying proportions of grog made from the same clay.

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[1] A. E. Dodd, *Trans. Cer. Soc.*, 1937, **36**, 64.

[2] *Refract. J.*, 1937, **13**, 63.

One of the most useful refractory materials for nozzles consists of a mixture of fireclay and bauxite in the proportions required to form sillimanite. The surface of such a material may be rendered more resistant to fluxes by heating it in a special furnace, such as that designed by Alleyne Reynolds, whereby the working face is heated to a temperature sufficient to form a very compact and partially fused surface without involving the expense of heating the whole brick or block to this temperature.

The clay and grog are ground in a perforated edge-runner mill, screened, mixed with water and pugged. Some manufacturers temper the paste in a pan after pugging it and before shaping; others temper it without pugging it. *De-airing* should be a great advantage, as it produces tougher and denser articles and greatly facilitates the shaping, but some firms have found it useless. Some manufacturers allow the paste to "sour" for a week or more. The paste may be shaped by hand-moulding, extrusion, or pressing in hand- or power-driven presses.

The use of sintered *magnesite* in the nozzles and stoppers of basic-steel furnaces has proved very satisfactory and they are, for such furnaces, more durable than fireclay, particularly when used with molten manganese steel. The high thermal conductivity of magnesite tends to draw heat from the metal, part of which "freezes" and blocks the nozzle.

Nozzles of *chrome-magnesite* mixtures (p. 525) have not been very satisfactory, and chromite nozzles are poor, so that fireclay and graphite mixtures are still regarded as the best.

Nozzles of zirconia were found to be satisfactory, but their cost has prevented their extensive use.

Other materials used for this purpose have the same composition as bauxite bricks or chromite bricks. Silicon carbide has not been used to an appreciable extent. "Sillimanite" appears to be unsuitable for some furnaces, but has been used satisfactorily in others.

The most important characteristics of outlets and stoppers are their durability and the accuracy with which they fit each other, as badly fitting stoppers are almost useless and last only a short time. They may be made of almost any high-grade fireclay, provided it is opened up sufficiently with coarse grog to withstand sudden changes in temperature.

It is essential that the central bore should be accurate in size, as an error of $\frac{1}{16}$ inch may cause serious damage.

The construction of the internal screw near the lower end of a stopper requires special care. In some cases the stopper should be built up in sections so that the portion containing the screw can be made separately in a hand-press.

The drying usually occupies several days. These articles were formerly burned in down-draught kilns, but in recent years the most progressive firms have used semi-muffle tunnel-kilns.

Stoppers and outlets are best burned at high temperatures, those corresponding to Seger Cones 10 to 12 being suitable, but it is not necessary, as some founders maintain, that they should be flashed and flame-stained. The only value of the stain is in showing that the two pieces have not been ground to fit each other—a process which destroys their surface and reduces their value unless they are of unusually good clay.

The material, when burned, should have a uniform and rather fine texture with very small pores. A high refractoriness is much less important than resistance to corrosion and abrasion. These articles are corroded or worn away so rapidly that most users prefer relatively cheap ones made of fireclay to much more expensive ones made of other materials. For this reason, zirconia, which has a high resistance to corrosion, is seldom used. On the other hand, if the materials are not sufficiently refractory and the nozzle and plug or stopper begin to fuse where they are in contact with each other, the resulting weld may become so strong as to involve considerable risk of loss of life to the workmen who endeavour to separate them whilst the furnace is at work.

Plugs are usually made of ordinary fireclay, but it is preferable to make them of a clay and grog containing at least 35 per cent. of alumina. They must be accurate in size and shape and so well-burned that they do not shrink appreciably when in use. Their properties should be the same as those of stoppers.

The cost of nozzles, runners, stoppers, sleeves, and other similar articles could be greatly reduced if fewer patterns and sizes were in use. This can only be arranged by agreement between manufacturers and users.

For further information see under "Ladles," p. 781.

Rod covers and *sleeves* are made of the same materials as stoppers and nozzles. Their texture is important, so that they can resist corrosion and sudden changes in temperature; it must be homogeneous and free from laminations. They must be perfectly straight with accurately shaped ends and must be of ample thickness. They must be well burned, so that they do not show any serious permanent expansion or contraction at 1450° to 1600° C., but must not be over-burned, or they will tend to spall and be too sensitive to rapid changes in temperature.

Tubes, pipes, troughs, funnels, and *tuyères* are made of fireclay in moulds of plaster or wood. It is, however, customary on the Continent to shape them roughly by passing the clay-paste through a pipe-press, and then to re-press to the proper shape. In this way, the appearance of the article is improved, and the second pressure makes the clay more dense and, therefore, more resistant to slags and abrasion. This treatment is also said to enable the goods to be fired at 100° C. above the temperature at which they would otherwise be finished. They may also be made like hollow blocks.

A. A. Granger has suggested the following mixture for highly refractory tubes:—

Corundum (7-mesh)	20 parts
,, (4- to 5-mesh)	15 ,,
,, grog (broken tubes 4- to 5-mesh)	35 ,,
Kaolin (les Eyzies)	10 ,,
Fireclay	20 ,,

A temporary bond may be added if desired.

The quality of the goods made of clay is greatly improved by *de-airing* the paste of which they are made.

Tubes and rods made of pure alumina, magnesia, or other pure oxide are made by extrusion through a steel die with an internal mandrel or core to form the inside of the tube. The process resembles that for making wire-cut bricks or sanitary pipes. As some of these oxides are highly abrasive, steel dies wear away rapidly at the point of extrusion. To avoid this the General Electric Co. use dies of artificial sapphire mounted in steel dies with cores of tungsten.

The paste used for extruding must consist of rounded grains, as highly angular ones lock together and will not pass out of the die. The maximum size of particles depends on the annular outlet of the die. The speed of flow must be regulated to suit the material and size of tube or rod. With very narrow dies a linear speed of 150 feet per minute may be used.

An ingenious device for extruding tubes has been described by D. Turner (*Trans. Cer. Soc.*, 1934, **33**, 47).

Interesting designs for tuyère-making machines are to be found in Eng. Pats. 3096 (1889) and 11,316 (1893). The author has found that extrusion, as described above, is usually quite satisfactory, as the "life" of a tuyère is limited more by physical damage than by any defect in its manufacture.

Pyrometer tubes and *cores for electric furnaces* have been satisfactorily made on a commercial scale of alundum united with a suitable bond and fired at Cone 14 (1410° C.). The bond is either a fusible clay, or a mixture of felspar and other fluxes with a refractory clay to produce the equivalent of a fusible clay. Similar tubes are made also of refractory porcelain (Chapter XVI.).

Pyrometer tubes made of "sillimanite," *i.e.* cyanite, calcined at 1450° C. and then ground and bonded with ball clay appear to be particularly satisfactory. All these tubes are made by extrusion from a vertical press. They may have a lug formed on one end from which they can be hung vertically to dry, or they may be dried on grooved boards. They must usually be dried in a vertical (hanging) position. According to Roeser[1] sillimanite tubes are superior to those of any other ceramic material.

A useful temporary bond for application in extruding tubes of pure oxides consists of:

Cellulose acetate	100 parts
Industrial spirit	200 ,,
Benzole	200 ,,
Acetone	700 ,,

Tubes of alumina and other pure refractory articles cannot be glazed in the ordinary manner, but can be given a glossy exterior by playing an oxy-gas flame over the surface to produce superficial fusion. For this treatment tubes which have been fired at so high a temperature as to produce a large proportion of recrystallised alumina are superior to others.

Some hollow-ware articles made of refractory clay may be *cast*, as described on p. 611; others must be built up wholly by hand in a manner similar to glass pots (Chapter XIII.).

The demands made on refractory hollow ware necessitate the greatest care being taken in its manufacture, as faulty goods may result in very serious financial loss to the user and may also cause disastrous accidents or even loss of life.

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[1] *J. Res. Bur. Stand.*, 1931, pp. 485–494.

CHAPTER X.

SAGGARS.

SAGGARS (fig. 113) are open boxes or trays made of refractory material and used to contain tiles, porcelain, and other pottery, etc., when the latter is heated in a kiln or oven. The purpose of saggars is to protect their contents from the action of flame, ashes, smoke, and objectionable gases, and to afford a convenient means of supporting the goods. The heat from the kiln is absorbed by the saggars and is radiated on to their contents without the deleterious results which would occur if the goods were heated in an open kiln.

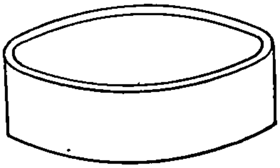

FIG. 113.—Saggar.[2]

Saggars are usually circular or oval in shape, though square and rectangular ones[1] are sometimes used. They may be of any convenient size and shape, and it is desirable to have a large number of saggars of different sizes and depths suitable for the goods to be burned. If the saggars are too large or too high, much space will be lost in the kiln; if they are too small, they will be useless.

The commoner sizes of saggars in general use are—

Oval (general) 20 inches by 15 inches by 8 inches.
(for ewers) 20 inches by 15 inches by 16 inches.
(for cups) 20 inches by 15 inches by 4 inches.
Round (general) 20 inches diameter; 5½ inches high.
(for basins) 20 inches diameter; 13 inches high.
(for plates) 14½ inches diameter; 7 inches high.

In use, saggars are filled with unburned ware and set one on top of the other, so that the bottom of one forms a cover for the one below it, the joint between the two being closed by a strip of " wad " clay.

Sometimes the bottom of the saggar has a hole in it so that the bottom of the basin or similar article in it may project into the saggar below. In this way a considerable amount of space (" height ") may be saved. For very tall articles, bottomless saggars—termed " ringers "—are placed on the ordinary saggars.

The walls of saggars are usually ½ inch to 1 inch in thickness. If sufficiently strong, the thinner the wall the better the saggar, as thick walls do not let the heat pass so readily, occupy more space in the oven, require more material,

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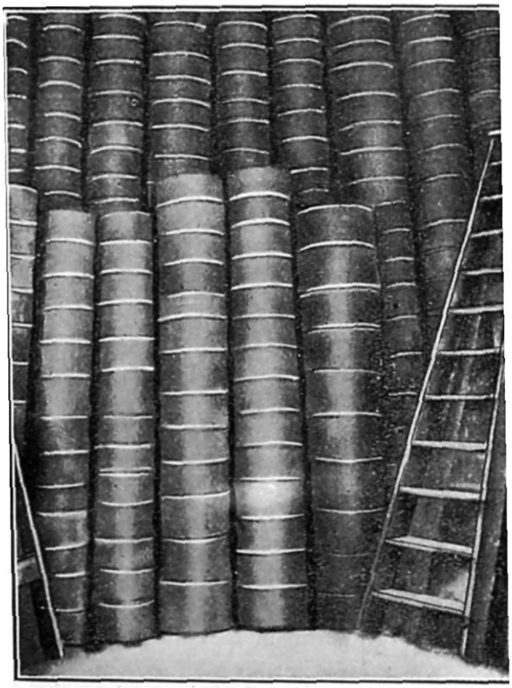
[1] Rectangular saggars must be placed so as to leave ample space for the oven gases to pass around them. With round or oval saggars this space is provided automatically.

[2] An alternative spelling is "sagger."

crack more readily, and are far less durable than saggars with thinner walls. Some firms use thicker saggars for those parts of the kiln or oven in which the flames impinge directly on them. Many saggars are much too thick, and by reducing the thickness slightly a considerable saving, both in fuel and saggar-material, may be made.

The saggars are piled one above the other in columns; each column of saggars forms a *bung*, and the bungs are arranged in *rings* (fig. 114).

The bottoms are usually rather thicker than the sides, so as to enable them to carry the weight of the contents of the saggars. The bottoms are usually flat, but in some Continental works they are made to slope slightly downwards towards the centre, but become flat when the saggar is burned. In some German works, the saggars are used in an inverted position and the upper surface is made level by coating it with a mixture of four parts of saggar paste and one part of plastic clay. It is stated that this coating also prevents the saggar from bulging.



(By courtesy of Messrs. Copeland & Sons.)

Fig. 114.—Saggars in position in oven.

Some firms prefer saggars with perforated bottoms.

J. P. Guy has found that saggars with corrugated sides and bottoms[1] are more durable than flat ones, just as a corrugated pipe or boiler is stronger than a plain one.

The bottoms are usually fixed to the sides, the saggars being in one piece, but many attempts have been made to use loose bottoms. There are obvious

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[1] Registered design 646,717, 1915.

advantages in this, but they are largely counterbalanced by the difficulty experienced in getting the rings and bottoms to fit accurately when both have been used several times. In the manufacture of abrasive wheels, loose rings and bottoms have proved quite satisfactory provided they are both made sufficiently thick to resist warping. In one works, such saggars up to 16 inches diameter can usually be burned fifty times and larger ones about twenty times at a temperature of about 1400° C. Instead of separate bottoms and rings some firms prefer one-piece saggars with a dished bottom into which they fit a loose plate which can easily be renewed.

Materials.—Saggars are usually made of fireclay and grog, but silica may be used for small ones.

According to J. P. Guy, *fused silica*, such as that made by the Thermal Syndicate, Ltd., is "an ideal material for saggars, being light, strong, and fire-resisting." It can be made into any desired shape and "will not warp under any ordinary heat or weight." It can be made into saggars with walls only $\frac{3}{8}$ inch thick and with bottoms equally thin if bearers are provided, thereby affording great facility for the transmission of heat to the goods in the saggars. The author has had no experience of saggars made of fused silica, but from a lengthy experience of that material made into other articles he finds it difficult to believe that the foregoing statements are correct if applied to the burning of china and earthenware, unless means can be found to screen the saggars from the direct action of flame. It is true that the temperature inside the saggars in a china oven is some 250° C. below the softening-point of fused silica, but the flames to which the outside of the saggars is subjected are often far hotter and would be almost certain to cause warping or even the collapse of the lower saggars.

Apropos of silica as a material for saggars, it is interesting to note that its use for this purpose was patented in 1877 by E. Robins, who used siliceous rock particles bonded with water-glass. It was found, however, that saggars made in this manner collapsed suddenly after they had been in use for a short time—possibly owing to changes in the crystalline form of the silica; such changes could not occur with fused silica unless the latter was converted into cristobalite.

Aluminous asbestos, or a mixture of asbestos and alumina, was patented by J. P. Guy in 1888, but has not been extensively used. According to the patentee, good saggars with very thin walls have been made of this material bonded with sewage sludge or fireclay.

Corundum (or highly burned *bauxite*) mixed with a little binding clay appears to produce excellent saggars, but is too costly for general use. Saggars made of *fused alumina* and used at Cone 12 have proved much more durable than those made of fireclay.

Clays.—According to the purpose for which the saggars are used, the fireclay may be of best or inferior quality. A local fireclay is used as far as possible, as it is unremunerative to make saggars of clay on which a high charge for carriage has been paid.

A good saggar clay must be highly refractory, uniform in texture, and have a good binding power, so that it will take up a sufficient quantity of grog. In Great Britain, the fireclays of the Coal Measures are used, but on the Continent a more plastic material, somewhat corresponding to the Dorset and Devonshire ball clays, and with a composition very closely resembling china clay, is preferred on account of its greater binding power and purity. A clay which is too fat is not satisfactory, as it usually shrinks excessively.

It is an advantage in a saggar clay if it can be burned at a moderate temperature and afterwards used in the kiln or oven without further serious shrinkage. An ideal binding clay vitrifies, or burns dense, at Seger Cones 1 to 3, but does not lose its shape below Cones 30 to 32.

As no single clay possesses all the properties requisite in a saggar, it is usual to mix two or three different clays or seams of clay together in proportions which depend on the clays used. For saggars, a mixture of clays is preferable to the use of a single clay. Thus, the addition of a ball clay to supply the requisite binding power has a great advantage, as it gives a much more durable product. For example, saggars composed wholly of fireclay are mechanically weak and crack after a few firings, but when a suitable addition of ball clay is properly made, the saggars last indefinitely and are only broken in handling. When only one clay can be used, a good Staffordshire or Warwickshire fireclay or saggar marl will meet most requirements, and for saggars it is as near perfection as can be reached with a single clay.

One of the great difficulties the saggar manufacturer experiences is in getting a mixture of materials of the necessary refractoriness. The fact that the Staffordshire clays have been used so long and with some amount of satisfaction makes potters very loth to change to other materials. Yet, it is an undoubted fact that the Staffordshire clays are less satisfactory than some Continental ones because they lack heat resistance, on account of the impurities they contain. They are only of moderate plasticity, so that with a sufficient proportion of grog to make them withstand repeated heating and cooling they must be made with thick sides and bottoms in order that they may possess the necessary mechanical strength. See later under *Refractoriness.*

Complaints are often made that the saggar marls now used are not so good as those formerly employed. As the same seams are still available, such differences as exist are probably due to the greater care which used to be taken in selecting and treating the marls. For some years, potters have paid so much attention to obtaining low-priced saggars that many of them appear to have overlooked the fact that one of the great secrets of successful manufacture depends on the careful selection and manipulation of the saggar marls, and that an excessive striving after cheapness may eventually prove to be most wasteful. A careful examination of the ordinary saggars now used, with pieces of those employed about a hundred years ago, will convince any unbiassed potter that there is less iron in the old saggars and that their texture is more uniform than that of the present ones. This is probably due to the use of weathered clays.

If the clays or marls used are not selected with sufficient care, they will be too rich in iron compounds[1] which lead to discoloration of the ware and to a reduction in the durability of the saggars. It is, therefore, a wise policy to pay a good price for the clay or marl and to insist on its being carefully selected and properly weathered. Saggars made from siliceous clays have a great advantage over those made from highly aluminous materials in being more resistant to loads at high temperatures, and when properly calcined they have a greater permanency of volume, but are more sensitive to sudden changes in temperature.

A mixture suggested by M. R. Hornung as suitable consists of—

50 per cent. of raw clay,
20 per cent. of calcined flint clay, and
30 per cent. of chert.

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[1] S. T. Wilson has found from 10 to 14 per cent. of ground nodules in various marls supplied in the ground state. These are the chief fluxing agent in the Staffordshire marls.

Chert is more satisfactory than quartz for siliceous saggars, and fine-grained materials are preferable to coarse ones. The siliceous material should be calcined before making it into saggars, as this treatment lessens the tendency of the material to spall.

The weathering of the clays used for the manufacture of saggars is extremely important and can hardly be overdone. In fact, the small amount of weathering to which some clays now used are subjected is one of the chief causes of so many of the present-day saggars being less durable than those made many years ago. When a clay has been properly weathered, any pyrite or siderite nodules are made more clearly visible and may be more easily removed in the *sorting*, which should always precede the grinding of clay for saggars.

In order that the clays may be properly ground they should be carefully *dried* before use. Air-drying in a warm room is preferable to the use of an artificially heated dryer, as the latter may easily spoil the clay by overheating it.

The author has frequently observed that the material ground in old and almost worn-out mills contains less impurities than that from a newer mill. This appears to be due to the harder impurities not being ground so readily as the clay, and confirms the wisdom of those potters who clean out their saggar-clay mills twice a day.

In addition to sorting the clay, some method of *cleaning* it (especially with a view to the removal of the iron compounds missed by the sorters) should be used, though this is seldom done at present. One of the methods described on p. 256 should be helpful.

The clay or clays must be ground before use, as described on pp. 261 to 270.

The clays used are usually of two kinds:

(i) *Base clay*—generally a fireclay, such as Staffordshire marl, which when burned has a high porosity, low shrinkage at 1150° C. and constant volume at 1300° C. In this country such clays usually form the greater part of the saggar. On the Continent a material closely resembling *china clay* is used for the base clay and has several advantages over the fireclay used in this country. A high-class china clay is not necessary; an inferior one (if not too poor) would be quite satisfactory (see p. 562).

(ii) *Bond clay*—such as a ball clay, which when burned has a low porosity, sufficient vitrification to form a strong bond and yet sufficient refractoriness not to lose its shape unduly. Only a small proportion of bond clay can be used, or the saggar would be too dense and would crack.

Grog.—For saggars, the grog is generally made by grinding up the cleanest parts of old and broken saggars, a sufficient quantity of new grog, made as described on p. 141, being added as required. When glost saggars are used for this purpose, care should be taken that they are fairly free from glaze, for the latter, though valuable in small quantities for increasing the strength of the fired saggar, tends to reduce its ability to withstand high temperatures, and so detracts from its value. In cases where saggars scale or "fly," the addition of rather more glost saggar and rather less biscuit saggar to the clay mixture will often remedy the defect without seriously impairing the strength of the new saggars.

In using old saggars as grog, a possible source of weakness may arise owing to the property possessed by fireclay of crystallising after repeated heatings and coolings, and producing a material which has a strong tendency to split in certain well-defined directions. This weakening is the more pronounced, the larger the proportion of old saggars in the paste used for making the ne ones, and whilst there are no records to prove exactly what amount of dama can result from this cause, the majority of potters are aware that care m be taken not to include too many glost saggars in the material they grind up for grog. The reason is the same in both cases, the tendency of the fluxes (glaze, etc.) being to produce crystalline matter which is at once a source of strength and weakness—of strength in that it binds the materials together with a kind of glassy cement so long as it remains vitrified, but of weakness so soon as it begins to form crystals which not only have no binding power of their own but actually determine to some extent the directions in which fracture of the saggars shall take place.[1] In grinding saggars for the production of grog, it is important to have the particles as sharp and angular as possible, and the extremely fine meal with rounded particles is best separated by sifting and not used. The angular particles bind together in a much more satisfactory manner, and produce stronger and more durable saggars.

Sizes of Grog.—The question of the sizes of grog for saggars has long been a serious one, and although investigations have been carried out, most manufacturers continue to work on a rule-of-thumb basis. A little consideration will show that the best and strongest saggars will consist of a series of grades of grog, the particles of each succeeding grade being of such a size and used in such proportion that they fill up the interstices left by the previous grade or grades. Dust-grog must not, as a rule, be used, as saggars require to be porous in order to withstand the various changes in temperature to which they are subjected.

The size of the largest particles must obviously depend on the thickness of the walls and bottom of the saggar, but it is seldom that particles larger than $\frac{3}{8}$ inch could be used satisfactorily, and for thin-walled saggars the diameter of the largest particles should not exceed three-eighths of the thickness of the saggar wall.

Having thus determined the size of the largest pieces and eliminated as "dust" all particles less than $\frac{1}{32}$ inch diameter, the intervening sizes may conveniently be divided into three grades, namely: (*a*) *coarse grog*, having particles between $\frac{1}{8}$ inch and $\frac{3}{8}$ inch diameter, (*b*) *medium grog*, having particles between $\frac{1}{16}$ inch and $\frac{1}{8}$ inch diameter, and (*c*) *fine grog*, having particles between $\frac{1}{32}$ inch and $\frac{1}{16}$ inch diameter.[2] In the United States a popular grog consists of: residue on 3-mesh 0·6, on 4-mesh 24·5, on 6-mesh 31·4, on 8-mesh 22·2, on 10-mesh 11·6, on 14-mesh 5·8, on 20-mesh 2·6, and passing through 20-mesh 1·3 per cent.

The main disadvantage of using too large particles of grog is the brittleness produced in the saggars, rendering them easily broken, very fragile under sudden changes of temperature and less strong mechanically than those in which smaller particles are used. Grog too rich in fine particles tends to make the saggars unduly sensitive to sudden changes in temperature.

For large saggars or slabs, 4- to 20-mesh grog should be used up to about 50 per cent. Even a small proportion of fine grog has an adverse effect, except where the saggars are subject only to compression; fine grog may then be used with advantage.

S. T. Wilson has found experimentally that the size of grog does not alter the contraction during drying, but is influential in other ways; thus, coarse grog will make saggars which will stand repeated firings, but will not bear the

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[1] If the crystals form a felted mass of fine needles, they will usually produce a stronger material than the amorphous calcined clay.

[2] German grog is of two grades: *coarse grog* consisting of particles between $\frac{1}{25}$ inch and $\frac{1}{4}$ inch diameter, and *fine grog* consisting of particles less than $\frac{1}{25}$ inch diameter but free from dust. In France a somewhat finer grog is used than in this country, and separation is made into three sizes: (*a*) passing a 12-mesh sieve, (*b*) passing a 25-mesh sieve, (*c*) passing an 87-mesh sieve. This last size (though popular) is too fine for other than very small saggars.

weight of goods in or above them, whereas fine grog with a greater percentage of porosity will not stand temperature changes, but bears the weight very well. A mixture of both coarse and fine (not dust) grog gives the best results. The grog and clay used by English potters are not as refractory as is desirable, and, consequently, the saggars made from them only last a short time. This is largely due to imperfect selection and absence of purification of the clays, as the best specimens of clay are of ample refractoriness.

Talc or *steatite* may be added to the extent of 5 to 40 per cent.; it appears to increase the durability of saggars[1] by reducing the thermal expansion and increasing the resistance to sudden changes in temperature. Talc containing a little lime is better than pure talc.[2]

H. Thiemecke[3] has shown that the addition of not more than 15 per cent. of talc makes a clay-paste of better working power, and that the burned saggars contain more mullite and are stronger both when hot and when cold. Talc must not be used in large proportions in saggars employed at temperatures above Seger Cone 11 (1320° C.), as it then acts as flux. The talc or steatite appears to form cordierite ($2MgO.2Al_2O_3.5SiO_2$)—a mineral having a very low thermal expansion.

Fused-alumina is devoid of plasticity and cannot be used alone in saggars, but it may be added up to about 30 per cent. to an ordinary saggar mix, though it will probably require the substitution of some of the fireclay by a more plastic clay, such as ball clay. Fused alumina (corundum) increases the resistance of saggars to sudden changes in temperature, but it is expensive.

Magnesia when present in very small proportions has the same beneficial effect as talc or steatite.

Olivine and *serpentine* have a similar effect to steatite.

Sillimanite (*i.e.* calcined cyanite) and allied materials appear to produce particularly durable saggars if a suitable ball clay is used as a bond, or they may be used as a substitute for grog.

Silicon carbide (" carborundum ") is an excellent " grog " for saggars, but the proportion must not exceed about 60 per cent. of the whole, or the contents (ware) may be stained (see p. 577).

Reducing atmospheres have an adverse effect on carborundum saggars.

Care should be taken to use the best crushed carborundum; the material called *carborundum sand* is often useless, as it is not pure carbon silicide.

Zirconia has not proved satisfactory.

The use of *china pitchers* (broken pieces of biscuit porcelain) in place of some of the grog has been found to increase the durability of the saggars. The respective value of dense and porous grog in saggars was investigated by L. Parthonnaud in 1913, with the result that a mixture of 70 parts of saggar clay and 30 parts of pitchers was found to produce saggars of exceptional durability. The pitchers must be ground and graded in a similar manner to grog. Some years previous to Parthonnaud's work, it was well known in Staffordshire that the use of china or earthenware pitchers as grog was better than the exclusive use of broken saggars, but few firms appear to have made much use of this knowledge.

Silica, in the form of *sand*, *quartz*, and *flint*, is unsatisfactory as an ingredient of saggars, and materials containing it should be used with great care. The object of adding such materials is to reduce the shrinkage. The objection to their use is due to the silica expanding whilst the clay contracts on burning, thus setting up two different kinds of stresses in the saggar and

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[1] *J. Franklin Inst.*, 1934, pp. 623–624.

[2] *Bull. Amer. Cer. Soc.*, 1935, **14**, 12.

[3] *J. Amer. Cer. Soc.*, 1934, **17**, 2.

correspondingly weakening it. This objection may not apply so forcibly to the addition of 30 per cent. of *calcined chert*, in which, according to M. R. Hornung, the transformation of the silica is completed during the first time of burning the saggar.

Fused quartz may be used as grog in saggars, as it does not suffer from the drawbacks of other forms of silica, though the particles are liable to be too smooth for the binding agent to adhere well. B. J. Moore states that the use of 50 to 60 per cent. of fused quartz produces very durable saggars, and also prevents dunting on rapid heating and cooling. He states that such saggars can be produced at low cost, but some users have found that saggars containing fused quartz " go rotten " after 3–5 firings.

Steatite and *Talc.*—The durability of fireclay saggars may be greatly increased by adding up to 10 per cent. of finely powdered steatite, which reduces the coefficient of expansion—possibly by forming cordierite (p. 234).

Heindl[1] found that the same amount of magnesia as is contained in the steatite or talc had the same effect on the expansion, but did not reduce the refractoriness so much.

Proportions.—The proportions of grog and clay used in saggars should depend largely on the binding power of the clay. The proportion of grog should be as large as possible consistent with the necessary strength, as this keeps the burned material " open," allowing it to stand sudden variations in temperature more readily and minimising the contraction.

The exact proportion depends on the nature of the clays used, some clays only permitting one-fifth of their weight of grog to be added, whilst others can be mixed with nearly an equal weight of grog, and a few clays are sufficiently plastic to enable twice as much grog as clay to be used. Lean clays can only stand the addition of comparatively small amounts of grog.

The proportion of clay required should be that which is required to coat every particle of grog with a plastic cement of just sufficient thickness to cause the grog particles to adhere and form a mass of the requisite strength. Consequently, the proportion of clay which should be used must depend on its plasticity and on the total area of all the non-plastic particles. So far, no one has been able to ascertain, on strictly scientific lines, any method of determining the actual percentage of any given clays which should be added, so that manufacturers are compelled to resort to trials which should be made with due consideration of the foregoing facts. On the whole, the figures mentioned above will be found satisfactory and typical, though they are not sufficient to meet the needs of all users or makers of saggars on account of the great differences in the plasticity.

An excessive proportion of grog so weakens the mixture that the saggars will not last sufficiently long to be serviceable, and in practice, a compromise must be effected between the loss due to the strains of temperature changes, and those due to mechanical weakness. The latter may be remedied by reducing the proportion and size of grog, but this reduction makes the saggars more sensitive to sudden changes of temperature.

In Great Britain, some firms do not have more than 1 part of grog to 3[2] parts of fireclay; but on the Continent, equal parts of grog and clay, or 2 parts of clay and 3 parts of grog, are generally employed. German saggar manufacturers employ 1 part of fine grog, 4 parts of coarse grog, and 3 to 5 parts of clay.

For large saggars coarse and medium-sized grog should be used, but for small saggars small-sized grog may be used. Some firms have found equal

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[1] *J. Res. Bur. Stand.*, 1935, **15**, 258.

[2] Other British firms use much more grog.

quantities of fine and coarse grog to be satisfactory; others use 3 or even 4 parts of fine grog to 1 part of coarse grog.

The use of raw kaolin in addition to plastic clay and grog is also customary on the Continent; it provides fine particles of a feebly plastic character, and the quartz in it reduces the shrinkage of the mixture. The chief value of kaolin (or china clay) in saggar mixtures is its power of producing a porous and refractory material with little shrinkage. As the particles are very small and the material expensive, too large a proportion should be avoided, but the addition of 10 per cent. of kaolin, or china clay, often greatly improves the quality of saggars. B. J. Moore recommends a mixture of 3 parts of china clay and 1 part of ball clay as a suitable binder for saggars in which 50 to 60 per cent. of carborundum or fused quartz is used as grog. If the saggars are to be used at temperatures lower than Cone 9 (1280° C.), a greater proportion of ball clay and a small one of china clay is required.

The following compositions are used by several German makers of saggars:—

TABLE LXXXVII.—COMPOSITION OF GERMAN SAGGARS.

	I.	II.	III.	IV.	V.	VI.
Saggar clay	30	20	20	20	75	60
Fireclay	..	..	10	30	..	30
Raw kaolin	15	20	15	15	..	..
Grog between $\frac{1}{32}$ and $\frac{1}{8}$ inch	40	45	55	35	15	10
Grog between $\frac{1}{8}$ and $\frac{1}{4}$ inch	15	15			10	..

A popular American saggar mixture consists of—

1 volume of Ostrander white clay.
1 volume of Tennessee ball clay.
1 volume of grog made of a mixture of the above clays in equal parts.

The grog is graded so that—

10 per cent. of it is left on a No. 4-mesh sieve.
20 „ passes through a No. 4 „
15 „ „ „ No. 6 „
12 „ „ „ No. 8 „
19 „ „ „ No. 12 „
12 „ „ „ No. 40 „
10 „ „ „ No. 80 „
2 „ „ „ No. 120 „

It is usually advisable to make the bottom of the saggars of a less plastic paste and one richer in grog than that used for the sides. The following are typical of mixtures now used in the Staffordshire Potteries:—

TABLE LXXXVIII.—COMPOSITION OF STAFFORDSHIRE SAGGARS.

Material.	For Saggar Sides.		For Saggar Bottoms.	
Peacock marl[1]	40	13	11	50
Littlerow marl	20	20	17	..
Bassymine marl	10	27	22	25
Broken saggars (grog)	30	40	50	25

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[1] This may be replaced by another siliceous clay.

It was found, many years ago, that a suitable mixture of Staffordshire saggar clays consists of—

Cane or Bassymine marl	2 parts
Black marl	1 part

and this or similar mixtures have been used for several generations.

Turner and Minton, in 1839, patented the use for saggars of a mixture of—

Dorset clay (ball clay)	6 cwt.
Grog (old saggars)	4¼ cwt.

The old potters were well aware of the principle of using a refractory material and a highly plastic bond, though some modern ones do not appear to realise its advantages. A careful study of the subject shows clearly that the *best mixtures* for saggars contain as much grog as possible.

A mixture suitable for making saggars must be sufficiently refractory, whilst at the same time it should possess ample strength if burned at a low temperature.

Mixing.—The saggar mixture must be carefully made, for, unless it is uniform in texture, it will shrink irregularly and will twist.

The most satisfactory method is to spread the various materials in a dry state in layers, one on top of another, to a height of 18 inches, and then to dig this over repeatedly, sprinkling it with a little water to keep down the dust. This gives a moderately good mixture, which is improved by passing it twice through a pug mill in which water is added, so as to produce a paste. This paste is piled up into a heap, beaten with wooden mallets to consolidate it, and is then allowed to stand in a cool place for several days to sour; after this it is again passed through a pug mill. If china clay is used in the mixture, it is advisable to mix the fireclay and grog together first, then to add the china clay, re-mix, and, finally, to add the water.

An alternative method of mixing consists in adding sufficient water to the clay and grog to make a thin slurry and to treat this in a blunger. The mixture is then run into a hot tank or on to a hot floor to drive off the superfluous water and to produce a paste which is afterwards passed through a pug mill. Unfortunately, most of the advantages conferred by this method of mixing are lost by the separation which occurs in drying the slurry. Hence, the chief benefit gained by this method is a very slight increase in the plasticity of the mixture due to heating it with water, unless the saggars are *cast* in a manner similar to glass-house pots (Chapter XIII.).

In another method of tempering, the ground materials are soaked in water for several days and are afterwards well mixed by means of spades; the mixture is then treated in a pan mill (fig. 46) for about twenty minutes. When it is desired to avoid soaking the mixture of materials before mixing, the clay and grog may be ground to the requisite fineness in an edge-runner mill, and, before adding water, they are passed through a suitable dry mixer, after which the required amount of water is added and the paste passed through a double pug mill and auger or wire-cut brick machine, the extruded clay column being cut into suitable lengths and made up immediately into saggars. Better working properties may be obtained by storing the pugged clay, covered with wet cloths, for several days.

The addition of sodium silicate (water-glass) to saggar mixtures is sometimes advantageous, as it reduces the amount of water necessary to make the material plastic and increases the strength of saggars during drying and the earlier stages of burning. If the proportion of water-glass is kept sufficiently low, its influence in lowering the refractoriness of the saggars is less costly than the amount gained from the use of saggars which are stronger when cold or only moderately heated.

It is essential that the mixing and tempering shall be thorough, so as to produce the maximum homogeneity in the mixture. When grog is used, it should be soaked in water some hours before it is mixed with the other materials, or the distribution of the water will be very irregular. Some firms find that better saggars are obtained by mixing the clay and grog together in the dry state and afterwards adding a sufficient amount of water and re-mixing.

Some firms in the Potteries find that it is more profitable to buy a " saggar mixture " and not to prepare one for their exclusive use. The purchased material, being made on a larger scale of material purchased under favourable conditions, is usually superior in quality to that made in a small pottery.

Souring.—Most saggar mixtures are greatly improved if the pugged paste is stored in a warm place for a week or more, and then re-pugged before use. Such storage effects a more perfect distribution of the water, and enables various reactions to occur which result in a stronger saggar than would be produced from the same material without any " souring " or storage such as that just described.

Saggar mixtures which are deficient in plasticity are improved by storage and by the addition of a larger proportion of plastic clay, or by the replacement of a lean clay by one of a more plastic nature, such as ball clay.

After souring, the material should be re-mixed in a pug mill.

Consistency.—A fairly stiff paste should be used for hand-made saggars, as a soft paste tends to warp and shrink too much. A stiff mixture is more difficult for the saggar maker, but the quality of the saggars is superior, as the more water the mixture contains, the greater will be the shrinkage in drying and firing, and the greater the risk of warped and twisted saggars.

The clay used in a saggar-making machine should be as stiff as the machine can use. It should have been most carefully prepared beforehand, as it is a mistake to expect the machine to mix the material as well as make the saggars. Material for use in saggar-making machines need not be so plastic as that used for hand-shaping, *i.e.* it can contain more grog or other non-plastic material.

De-airing.—The passage of the paste through a de-airing machine greatly improves its working qualities, especially if an extrusion press (fig. 118) is used for shaping.

Making.—Saggars are usually made by hand on a wooden mould or drum, but in recent years the use of power-driven saggar presses has increased.

For hand-moulding a little grog-dust[1] is thrown on to a board placed on the bench, and an iron ring[2] or frame rather larger than the bottom of the saggar is placed on it. A mass of paste is thrown into this ring and is beaten until it forms a solid slab. Any superfluous paste is removed by drawing a tightly stretched wire across the ring and lifting off the cut portion. The ring is then removed, leaving a slab a little thicker than the bottom of the saggar. Meanwhile, another workman, using two strips of wood fixed to another part of the bench, makes a band of paste of sufficient length to form the sides of the

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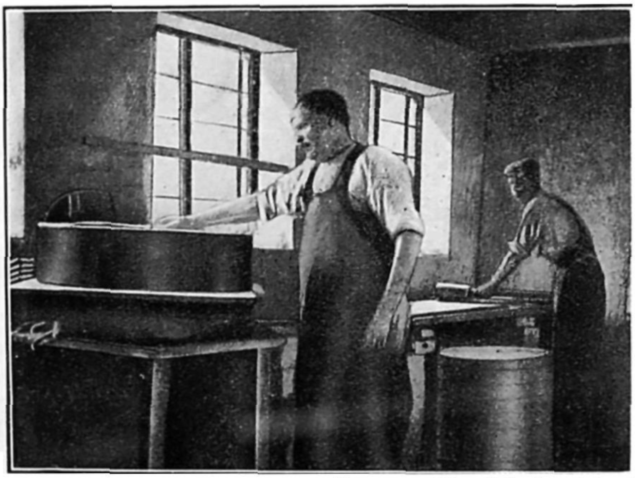
[1] Some makers use sharp sand or sawdust, but grog-dust is generally preferred for preventing the clay from sticking to the bench. Sand or fine grog sometimes flies off during the firing and so spoils some of the goods, whilst the sawdust is burnt off in the first firing of the saggar and can do no harm when the saggar is filled.

[2] One is shown hanging near the window in fig. 115.

saggar and of the same thickness as the wooden strips; he beats this well,[1] "strikes off," lays the band of paste on the drum and then winds it around the mould. The ends of the strip are cut off and joined by kneading the paste together. The drum and adhering clay are then placed on the slab or bat previously made, and the two pieces of clay are moistened and carefully kneaded together. This is done more easily on a revolving table than on a fixed bench. When a tight joint has been made, the superfluous paste is cut off and the surface is made smooth by means of a wet sponge or rubber applied whilst the saggar is revolved slowly. The drum is then removed and the inside of the saggar finished in the same manner.

The saggar is allowed to stiffen slightly, and is then examined and any irregularities removed; during this process it is turned over and the bottom is scraped level or is otherwise made of the desired shape (see fig. 115). After this, the saggar is set aside to dry.



(By courtesy of Messrs. Copeland & Sons.)

FIG. 115.—Making saggars by hand.[2]

Throwing on a potter's wheel is common in some Continental works, but is not much used in this country.

A still cheaper method consists in making the saggars in a plaster mould mounted on a jigger and turning the inside by means of a jolley or profile (fig. 131), in the same manner as dishes and basins are made of pottery. This method requires a softer paste than when a drum is used, and, as there are no joints to make, a less skilful workman can be employed. Its disadvantage lies in the cost of renewing the plaster moulds, which is serious, and in the softer paste employed, which shrinks and twists more than a stiffer one. The former disadvantage can be overcome by using a polished iron or steel ring and bottom plate in place of a plaster mould. Paper is laid on the

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[1] More than thirty years ago Messrs. Minton installed a machine for rolling and compressing the sides of the saggars so as to give them greater strength and to enable thinner sides to be used. This has proved very satisfactory (see p. 566).

[2] In fig. 115 the youth in the background is rolling out a strip for the sides of the saggar, and the man in the foreground is testing the bottom of the inverted saggar with a straight-edge.

plate and inside the ring to prevent the clay-paste coming in contact with the metal.

Saggars may be made by slip-casting in plaster moulds, like crucibles (p. 611) or glass-house pots (p. 651). They are regarded by some potters as superior to saggars made by pressing.

Evenness in the thickness of the sides and bottom of the saggars is very important; irregularities cause unequal distribution of heat and often set up serious internal strains in the saggars. To overcome this, the sides of the saggars may be rolled mechanically; by doing this, several firms have succeeded in increasing the durability of their saggars, whilst simultaneously making the walls thinner than heretofore.

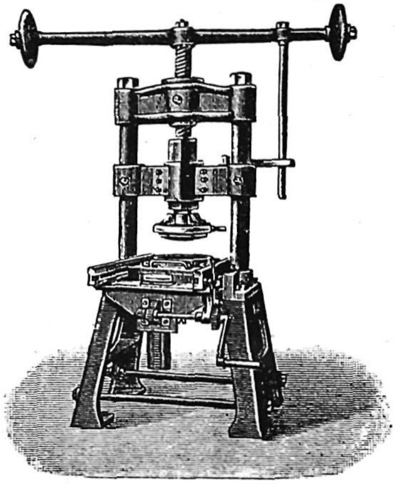

FIG. 116.—Hand saggar press.

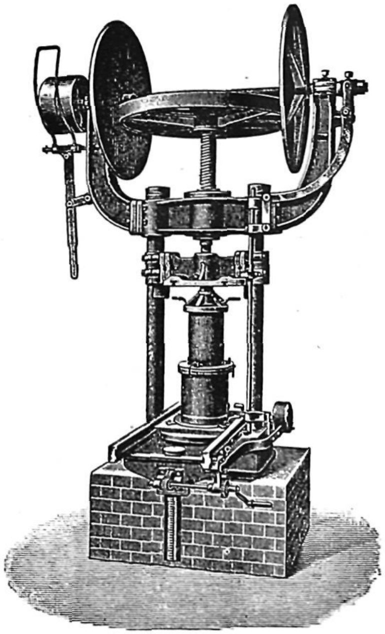

FIG. 117.—Power-driven saggar press.

Saggar presses are of several types; in some, the saggar is made complete; in others, a bat or slab of clay is laid in the mould and the machine fits the sides of the saggar to it, and in some works the bottoms and sides are made separately in a pipe-press and united by hand.

Screw presses (figs. 116 and 117) may be operated by hand for small saggars and power-driven for larger ones. The mould should be movable horizontally by means of a slide, and vertically by a rack and pinion, so as to facilitate the cleaning and filling of the mould and the removal of the saggars.

W. Boulton, in 1889, patented a press in which the clay is placed on a loose plate which rests on a bottom block and is surrounded by a movable mould; the mould is held fast, during the pressing, by a simple clamp. The plunger is forced down on to the clay by the action of the screw, and the clay is thereby forced into the desired shape so as to form the bottom of the saggar. The plunger is slightly raised so as to permit a flanged ring suspended from the plate of the plunger to retain it in position, and packing is then inserted between the ring and plate. The screw is then used to force the plunger again on to the clay, compressing it a second time, after which the plunger is raised by reversing the screw and the mould is lowered, setting the saggar at liberty, ready for removal.

The screw press patented by W. E. Gedge, in 1882, has a lifting screw fitted underneath the table which carries the clay, so that pressure is applied simultaneously from above and below.

In J. P. Guy's (1885) patent the saggar is made bottom upwards, the box of the mould being mounted on the screw and the male part of the die on the lower part of the press.

In the saggar press patented by F. Woodhead in 1895, the clay is placed on a rising table and forced by the latter into a mould fixed above it. When the pressing is completed, the return of the table automatically opens air-valves in the mould to prevent adhesion between the clay and the metal and, at the same time, an automatic stripper forces the saggar out of the mould on to the table.

Screw presses are usually worked by hand, as this enables the man working them to give a sharp sudden tug at the end of the stroke.' When driven by engine-power almost double the output can be obtained without materially altering the cost of production. Screw presses have the disadvantage that the pressure is applied too suddenly and for too short a time for the satisfactory production of such large goods, so that the saggars are not uniform in density and tend to crack when in use. Greater average density is obtained by pressing the saggar two or three times in rapid succession before removing it from the press.

The output of a screw press is greatly increased if it is fitted with a sliding table carrying three moulds, so that a man may stand on each side of the press and slide the moulds in turn under the plunger, losing the smallest possible time in the operations between each descent of the latter.

Toggle lever presses [1] are better than screw presses for saggars, but the height of saggar which can be made in them is so restricted that screw presses are often preferred, in spite of their drawbacks. To make tall saggars in a toggle lever press, the die should be capable of being lowered rapidly out of the way and as rapidly returned to its normal position when the clay has been inserted and all is ready for pressing a new clot. This saves much of the time usually lost in waiting for the lever operating the plunger to complete its motion, but it also involves considerable constructional difficulties.

The advantages of a toggle or crank-shaft press over a screw press are—(*a*) better leverage, (*b*) no screw to wear away, (*c*) less friction, (*d*) a rapid application of pressure at first, followed by a slow heavy pressure, (*e*) more uniform size of product, and (*f*) more uniform distribution of pressure on the article.

Presses with rotary tables (see fig. 53) have proved quite satisfactory for saggars of medium size and should also be good for large ones.

Hydraulic presses are only used for the largest saggars, and not extensively for these. One of the most satisfactory presses of this type is that patented by J. P. Guy in 1888 and improved in 1890 and 1899. In this machine, pressure may be applied simultaneously from above and below the saggar, or only from below it. In the improved form the mould is fixed; the clay rests on a plunger, and as the latter rises it is forced into the mould. The lower part of the mould is so long that the clay enters it completely before any pressure is applied to

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[1] A suitable modification of fig. 53 may be used.

it, thus ensuring the proper fitting of the mould and plunger and the complete filling of the former. Subsidiary rams for increasing the speed of the machine or for withdrawing the saggar are included in the 1899 patent. A stripper is fitted which automatically acts on the rim of the saggar and forces it out of the mould as the plunger descends. It is important to observe that in this machine the saggar is made in a normal position and not bottom upwards.

In all the foregoing presses, the mould is well lubricated with paraffin to which a little thicker oil, such as colza, is sometimes added. A lining plate to carry the saggar is usually inserted, and then a lump of the clay paste. The machine is set in motion and, after the pressing is complete, the saggar is carried away on the supporting plate [1] to the dryer. Before inserting a fresh plate and piece of clay the mould must be well lubricated. The great disadvantage of this method of working is the necessity of having a hundred or more bottom plates for the box, as the saggar cannot be lifted off the bottom plate, but must be kept on it until quite dry.

A good hand-operated press will produce about 200 to 250 saggars, each 20 inches by 15 inches or less, per day. Power-driven presses, such as those just described, have about twice this output.

The presses chiefly used for saggars in England are of the *extrusion type*, and are similar to those employed for drain pipes. The one patented by J. P. Guy in 1886 is typical, and consists of a vertical pug mill or extrusion machine which discharges its contents against a core in the mouthpiece. The mouthpiece is made in two pieces, so as to be readily removable from the saggar, and is extended, forming a mould for the outside of the saggar after the clay paste has passed the core. The moulding part of the mouthpiece can be raised whilst the saggar is being made, and lowered when it is complete. The saggar (which is made bottom upwards) is then cut off with a knife or wire. In other words, this machine is really a pipe press so modified as to form the bottom of the saggar as well as the cylindrical sides.

Leigh's patent steam saggar press, shown in fig. 118, has been in successful operation for a number of years. It is self-contained, occupying about 6 feet square of floor space, is 16 feet in height, and is driven by steam at a pressure of 80 lbs. per square inch. The largest size of saggar which this machine will make is one equivalent in area to a round saggar 21 inches in diameter. This machine, when working under favourable conditions, will produce six to seven hundred saggars per day of 10 hours, with a staff of four men, viz. one to feed, one to operate, one to fettle, and one to carry away the finished saggars.

The extrusion machine patented by J. Hamblet in 1888 consists of a vertical cylinder which is filled with clay; the latter is forced downwards by a power-driven plunger. This machine bears a close resemblance to pipe machines of the steam-press type. Like Guy's machine, it makes the saggar bottom upwards.

As steam presses of the intermittent pattern just described are slow in action, various engineering firms have adapted machines containing a screw feed in place of the piston or ram of the steam press. The Rawdon Foundry Co., Ltd., have been very successful with a machine of the screw-feed type, and as they use specially designed roller and ball bearings to take the thrust of the machine their saggar press works well with very little power.

In all saggar machines of the extrusion type great difficulty is experienced in making the bottom and sides simultaneously, an excessive amount of power being required for the former. In many cases it is better to make the sides and bottom separately, the former being made like pipes, by cutting off suitable

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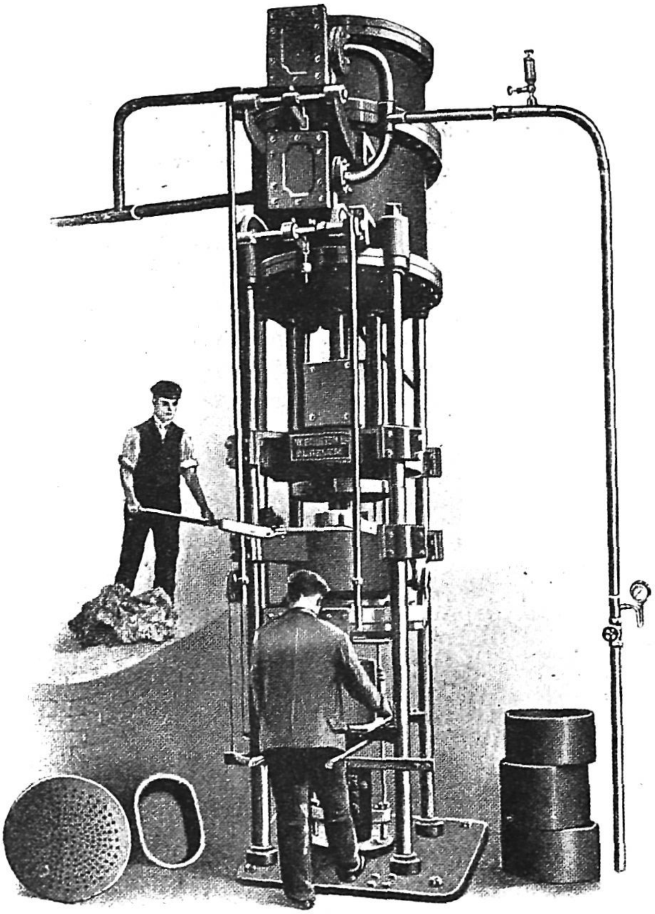
[1] Attempts to use plaster-supporting plates have not proved satisfactory.

lengths as they come from the machine, and the bottoms being made by cutting off a longer length of pipe, slitting this with a knife, opening it out flat, and fastening the sides or ring to it by hand.

A common error is to pass the clay too rapidly through the machine; the slower it travels the better, and the less power required. Another mistake is to overlook the presence of small projections in the machine, against which the clay is forced and stopped instead of passing steadily forward. Such projections are frequent when a machine is used for several sizes of saggars, the men merely changing the lower part of the die and leaving the bell intact. The result of this arrangement is that the clay is forced against one or more flat pieces of metal and remains there; it should, on the contrary, pass in a



Messrs. Wm. Boulton, Ltd., Burslem.

FIG. 118.—Leigh's steam saggar press.

steady stream from the inlet of the machine until it is given its new shape in the die or mould. The pressure exerted on motionless clay is all wasted, and it necessitates a serious increase in the amount of power required to drive the machine.

Casting.—The use of the slip-casting process (pp. 611–615) for saggars is yet in its infancy, but there are strong indications that it is of increasing importance. Cast saggars are stronger and more durable; they can be made of any desired porosity or density, but the initial cost is heavy.

Comparison of Methods.—Opinions differ greatly as to the merits of the six chief methods of shaping, viz. modelling, throwing on a potter's wheel, pressing in a modified pipe-press or a large screw-press, jiggering, and casting. On the Continent, throwing is the most popular method. The use of a " jigger " appears to offer several advantages over other mechanical methods, as the rate of production is increased, and a saving of about 35 per cent. in the time of making a saggar by hand or by throwing is effected. Various methods of pressing are also rapid, but the quality of the saggars is not usually so good as in hand-made, thrown, or jiggered saggars. The cost of cast saggars seems to vary so much in different works that it is difficult to say whether it is cheaper than the other methods; it is usually regarded as more expensive.

Marking.—It is desirable to mark each saggar with a number, so that a register may be kept. In this way it is easy to determine how many saggars are lost during each firing; 7 per cent. of the biscuit saggars and 6 per cent. of the glost saggars is the maximum loss allowable, a greater one being usually due either to defective saggars or to cooling the ovens too rapidly, *e.g.* in two days or less.

Drying.—Saggars are usually dried on racks in a room heated to about 30° C. by steam pipes placed under, or forming, the racks. The saggars must be carefully watched and should be turned occasionally to prevent them cracking. Very large saggars should be placed on boards which have been dusted over with clay, or on a bat of clay paste the size of the saggar; this allows the clay to " creep " during drying. If the boards or bats are placed on a steam-heated floor, the heating is less under control and the amount of floor space occupied is much larger than when racks are used.

A much more effective method is to use a dryer in which the humidity, temperature, and flow of air are all controllable. An American dryer of this type is shown in fig. 119. In a still more recent pattern the saggars are placed on shelves suspended from an overhead rail, on which they travel from the maker to the dryer and then to the kiln.

One of the chief difficulties in drying saggars is to avoid bottom-cracks by drying the sides too slowly and to avoid side-cracks by drying the sides too rapidly. It is, therefore, of great importance to control the temperature, flow, and humidity of the air in all parts of the dryer as fully as possible.

Transport.—Mechanical transport of saggars from the dryer to the kiln or oven is much cheaper than moving them by hand, and if the saggars are dried on suspended carriers their transport is effected at almost no cost. It is often convenient for each carrier to hold 24 saggars, on which they can be taken from the makers to the preliminary dryer, thence to the fettlers and the second dryer, and later to the kiln or oven.

Glazing.—In order to prevent the porous saggars from absorbing the glaze from ware placed in them, the saggars are usually coated internally with a glaze. Surplus glaze, or the " cleanings " of glaze tubs, etc., are generally used for this purpose, but a wash which has been used satisfactorily since 1843 consists of 13 parts of salt and 30 parts of potash dissolved in water and brushed on to the interior of the saggars.

Burning.—Saggars are usually burned in the kilns or ovens used for the goods to be placed in the saggars, *i.e.* in the biscuit oven, the empty saggars being placed on top of the filled ones. Where a multiple-stage oven is used, the new saggars may be burned in the uppermost storey. There are many drawbacks to both these methods, the chief one being that the saggars are incompletely burned, and so twist and warp when in use. The sole recommendation of the first method is that it is apparently cheap, the burning appearing to be effected without cost. For the best results, saggars should be burned specially. Those burned on the tops of the bungs are usually cooled too quickly and so do not develop the crystalline texture which would impart the maximum strength. This fact, so well known to Continental users of saggars, has never been appreciated by most English potters.

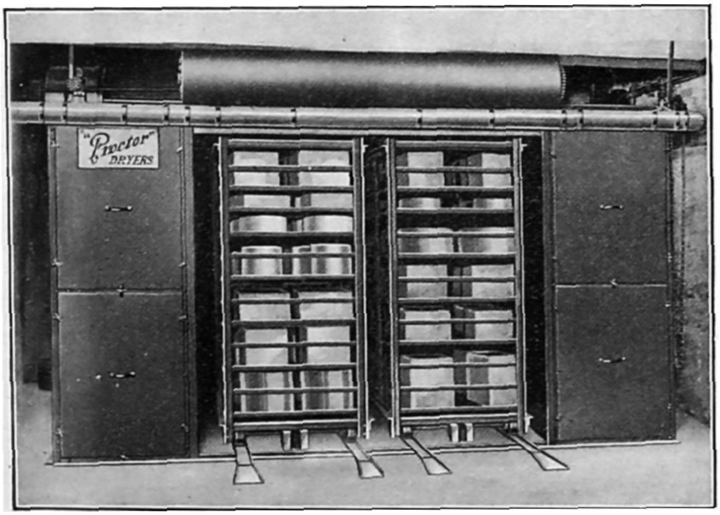


FIG. 119.—American tunnel dryer for saggars.

Some firms make saggars for sale; these must be burned in kilns built for the purpose. Potters' ovens are commonly used, but a continuous chamber or a tunnel kiln is more economical and is satisfactory in every respect. Saggars thus burned in special kilns are usually more durable than those burned along with pottery, as the latter are seldom fully burned.

Storage.—Saggars should be kept in a warm, dry place, where they cannot be affected by frost.

Properties.—The chief properties required in saggars are: (1) mechanical strength to resist the pressure of other saggars in the oven; (2) mechanical strength to resist the action of dust, etc., in the ovens and the wear and tear in placing and drawing; (3) density sufficient to withstand the reducing gases from the fuel, and to keep the goods free from discoloration; (4) resistance to high temperatures sufficient for the purposes for which they are required; (5) ability to withstand sudden changes of temperature due to local air-currents or sudden contact with a hot part of the flame; and (6) absence of contraction or expansion in the kiln to an extent sufficient to interfere with the contents of the saggars or to endanger the safety of the bungs.

Saggars vary greatly in the extent to which they fulfil these requirements, and it is by no means uncommon to find that two saggars made consecutively and apparently composed of the same material and treated in every respect in identically the same manner will behave quite differently in actual use, and one may easily last twice as long as the other. The properties just mentioned are dependent on a variety of others, of which the most important are as follows:—

Appearance.—Saggars should be as exact as possible as regards size and shape, so that they may fit accurately on each other. The inner surface should be smooth, and the texture—as revealed when a saggar is broken—should be free from irregularities and fissures. The thinner the saggars, the greater will be the amount of heat passing through them and the smaller the quantity of fuel required to heat the goods inside them. Unfortunately, saggars must be made rather thick in order to withstand the pressure of their contents and of the saggars above them.

Refractoriness.—It is not necessary that saggars should be very highly refractory, provided they are sufficiently resistant to heat to prove durable when in use.

The saggar marls of Staffordshire are quite satisfactory for saggars for the pottery made in the locality, but are useless for the higher temperatures required for the hard porcelain made on the Continent (Chapter XVI.). Hence, a saggar mixture with a refractoriness corresponding to Seger Cone 30 may have ample heat resistance for use in the manufacture of English china ware, but for hard porcelain a refractoriness corresponding to at least Cone 33 is required. The refractoriness as determined by observing the softening temperature is not the only kind of heat resistance required by saggars; a high collapsing temperature when loaded and a resistance to fire-gases, dust, etc., are equally important, as are also the following:—

Effect of Repeated Heating.—The effect of repeatedly heating saggars during use shows itself in two ways: (i) in the cracking of the saggars, and (ii) in their becoming misshapen to an extent which prevents them being used again. As the highest temperature at which saggars are used (Seger Cone 8 to 9 for earthenware and 12 to 16 for porcelain) is far below the softening-point of the saggars, the effect of repeated heatings at the above-mentioned temperatures is usually of much greater importance than the refractoriness or ultimate heat resistance; for a saggar which can be used repeatedly is more valuable than one which can only be used a few times, even though the latter shows an equal or better result on testing its ultimate refractoriness or softening-point.

The saggars used in English potteries only last fourteen or fifteen times, but the Continental saggars—which are used at a higher temperature—average fifty or more firings before they must be discarded. This difference is partly due to the English custom of using local fireclay (saggar marl), whereas the Continental potteries are usually some distance away from the fireclay deposits, and so are more careful to choose the best materials for their purpose. On this account also, they are willing to use a method of manufacture which English potters consider too costly, though the greater durability of the saggars made in this manner actually results in a saving as compared with the English method.

The shape of the saggars may prove to be of great importance with regard to their durability, and R. Seidel has shown that, whilst a square or rectangular saggar would be the best for many purposes, yet in order that it may resist the heat, the sides should not be flat but bulged internally or externally. Where a round or oval saggar is preferred, the chief difficulty is in the bottom bulging and so preventing the saggar being used for some articles. One method of preventing this bulging of the bottom is to coat the bottom of the saggar with a mixture of 4 parts of ordinary saggar paste and 1 part of plastic clay, preferably a ball clay, this mixture being applied after the saggar has been used once. The strengthening paste must be made some time before it is used, in order that it may be matured properly. It is applied to the saggar with the fingers and a trowel, it being necessary to press it well on to the saggar so as to ensure its proper adhesion, and any surplus paste should be removed with a properly shaped profile. If desired, the bottom of the saggar may be shaped so as to allow a part of the paste to be thinner or thicker than the rest.

The greater the uniformity in the thickness of the various parts of the saggar, the smaller is the risk of cracking. Thick parts should be avoided at all costs. The height of the saggar has a great influence on its durability, and it is always wise to use saggars of only one or two heights, and not a variety such as are generally used at the present time.

Reducing Conditions.—These often occur in ovens and kilns, and their effect must be borne in mind when considering the refractoriness of saggars. Any iron compounds present will probably be reduced to the ferrous state, and will then be converted into fusible ferrous silicates. The action is facilitated by the curious action of fireclay on carbon monoxide, accompanied by the deposition of carbon in the pores of the clay and by a disintegrating action on the brick.

Resistance to Corrosion, Slags, etc.—This is not an important property for saggars, though they must be sufficiently resistant to withstand the action of the ash, etc., in the fire-gases. In securing the other requisite properties, this one is obtained without further trouble.

Resistance to sudden changes in temperature is necessary, because saggars are placed in an open kiln, and are liable to exposure to eddies of hotter gases and to cooler air. They are also heated and cooled each time they are used. To secure this resistance, they must be porous; this is best obtained by the use of a sufficiently large proportion of grog.

Freedom from spalling or "flying off" is particularly important, as, if this occurs inside the saggar, it may damage the ware and cause a heavy loss. This defect is usually due to a faulty mixing of the saggar material, and is less liable to occur if a large proportion of the grog consists of old saggars; sand or crushed rock is particularly unsuitable as a substitute for good grog.

The cracking of saggars is commonly due to the use of a material which is too dense, on account of the material being too fusible, or to its being badly graded. It may be avoided by using a more refractory material, a larger proportion of grog, or a coarser grog than before. Saggars which prove of good value generally have a porosity of 12 to 14 per cent., but some saggars are so porous that they absorb 25 per cent. of their weight of water on immersion. There is no harm in a high porosity if the pores are sufficiently small to protect the contents of the saggar, and if the mechanical strength of the saggar is sufficiently great.

The cracking of saggars appears to be closely related to the linear thermal expansion, which in an ordinary fired saggar body is 0·47 to 0·55 between 15° and 1000° C. The addition of 5 to 10 per cent. of steatite reduces this to below 0·40, and it also reduces the expansion due to cristobalite. An excess of steatite must be avoided, or the saggars will be distorted when in use, as steatite is a flux.

The resistance to sudden changes in temperature may be predicted[1] by plotting:

(a) the factor $\frac{R}{E}=\frac{\text{modulus of rupture}}{\text{modulus of elasticity}}$ against

(b) the linear expansion up to a selected temperature (T).

For any given temperature, the saggars with the greatest resistance have a low modulus of rupture and a low modulus of elasticity. With the 70 American saggar bodies examined the most satisfactory had $T=780°$ C., $R=750$ lbs. per square inch and $E=1{,}510{,}000$ lbs. per square inch.

Mechanical Strength.—In order that saggars may have the necessary mechanical strength to permit their being piled in high bungs, they should be fired to a much higher temperature than that to which they will be exposed when in use. This is seldom the case with English saggars, and is one cause of their low durability. The minimum crushing strength permissible in saggars is about 3500 lbs. per square inch of solid material.

It is of the greatest importance that saggars should be sufficiently strong, as if one collapses it may " let down " nearly all the saggars in the same bung, and may also affect others. The value of the ware damaged in this way may be serious, and it may even happen that the oven cannot be properly finished, as the burner is unable to reach his " trials."

The statement that the Staffordshire saggar marls produce stronger saggars than those made of fireclay from some other districts is only true when the other fireclays have not been treated sufficiently to develop the requisite mechanical strength. The average compressive strength of pieces of saggar is 1340 lbs. per square inch. The failure of some saggars may, according to A. S. Watts, be attributed to the period of weakness occurring in the burning when the clay is dissociated and sillimanite is formed. If this is correct, highly siliceous materials are preferable for saggars to those made from flint clay and other clays which form sillimanite at a lower temperature and, therefore, tend to be weak at that temperature. It is more probable that the weakness is due to fused material than to the felted mass of crystals formed by sillimanite.

If a saggar, when cold, has ample strength, the lower the proportion of vitrifiable matter it contains the greater will be its durability.

Refractoriness-under-load.—It is essential that saggars to be used for biscuit should have ample refractoriness-under-load, so that they may support their contents and each other at the highest temperatures to which they are exposed when in use. Saggars for glost-ware need not be so strong at high temperatures, but they must resist sudden changes in temperature.

The refractoriness under a load of 50 lbs. per square inch should not be less than 1300° C.

Porosity.—The porosity of different saggars varies greatly: it should be moderately high to ensure freedom from spalling and yet should not be so high as to be a source of weakness. Usually, the best saggars have a porosity (water absorption) of 20 to 25 per cent., but these figures are not applicable to all good saggars.

Shrinkage.—Saggars must not shrink much in use, or they will twist and lose their shape, besides fitting badly on each other and tending to fall. A low shrinkage is obtained by the use of a large proportion of grog and by firing the saggars for a sufficiently long time at a higher temperature than

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[1] Heindl and Mong, *J. Amer. Cer. Soc.*, 1933, **16**, 601.

that at which they will be used. More saggars fail through shrinkage and excessive expansion than as the result of low mechanical strength.

Resistance to temperature changes is produced by the presence of a minimum of free silica, by careful proportioning of grog and clay, and by taking whatever precautions may be necessary to keep the linear coefficient of expansion between 0·10 and 0·15 per cent. between 0° and 250° C.

All saggars tend to become more brittle and, therefore, weaker after several repeated firings. The precise cause is not known.

Resistance to sudden changes in temperature is not related very closely to the porosity of saggars, though the latter has some influence.

Excessively rapid cooling causes much damage to saggars. Thus, observations in several works have shown that where only 24 to 72 hours were allowed for cooling, the saggars lasted on an average 6 to 11 times, whilst where the ovens were cooled in 168 hours the saggars lasted 50 times or more.

Cost.—Whatever good properties saggars may possess, it is essential that they shall be cheap. Yet the cost of individual saggars must not alone be taken as a criterion, for it is economical to pay a higher price for a saggar which can be used more frequently than another. Moreover, saggars which are cheap in first cost often damage a considerable amount of ware, and so prove dearer in the end. Hence, in comparing different kinds of saggars, the cost should be divided by the average number of times each can be used, as found by actual trial over a sufficiently lengthy period.

When saggars are made in the pottery in which they are to be used, it is often desirable to arrange a fixed wage for the upkeep of the saggars and the manufacture of new ones. By this arrangement, it is to the saggar-maker's interest to make the saggars well, whereas, if paid piecework, it is more to his interest to make poor saggars. Much of the expense of maintaining a good stock of saggars may be avoided by counting them repeatedly, by taking pains to see that a sufficiently large and varied stock is maintained, and by marking each saggar with a serial number and noting how long it will last.

The financial effect of even a small increase in the durability of saggars is very marked, and, as the saving effected by improving the quality and efficiency of saggars may easily amount to £500 a year, a careful and exhaustive study of saggar manufacture on the lines indicated should be remunerative to the user.

It would probably pay English potters to combine and erect a saggar manufactory in which the saggars would be made with a large proportion of highly refractory grog (possibly of china clay), united with a good binding clay, *e.g.* ball clay, and burned at Cone 14 to 16 in a special continuous chamber kiln or in a tunnel kiln. The great durability of such saggars should effect a handsome saving to the users. In a few instances where individual china manufacturers have paid special attention to their saggars and have made them under expert advice, the reduction in cost per annum has been remarkable.

Defective Saggars, apart from those damaged in use, are largely the result of errors in the selection of the materials, insufficient grading, wrong weights or measures, imperfect mixing, or the use of a paste too soon after it is made. It sometimes happens that the solid materials are rightly proportioned, but an excess of water in the clay paste will make the goods dry irregularly and may cause them to twist and even to crack. The paste should be worked as stiffly as possible and the jointing should be carefully watched. *Cracks* and splits are usually due to some of the foregoing errors, but may be produced as the result of too rapid drying or careless firing. If the cracks are near the bottom of the saggar the skill of the maker should be called into question, though even well-jointed saggars will crack along the lower parts of the sides if too quickly heated at first. *Twists* and warping may be set down to the use of a mixture too rich in clay and to careless drying, though occasionally a clumsy assistant will knock the saggars out of shape in carrying them, especially if they are rather too heavy for him to move alone. Breakage or weakening of saggars during drawing and setting can also be reduced by supervision and by attention to the wad-clay, which sometimes vitrifies and so necessitates destructive pounding in order to detach the saggars to which it adheres. Breakage in heating up during the first firing is very liable to happen if the saggars are not thoroughly dry before being placed in the oven, though some clays will stand rapid heating better than others. The same considerations apply to the expulsion of the combined water in the saggar clays at a red heat, as in this case also the steam may be liberated too suddenly. Breaking during cooling is probably the predominant cause of loss in saggars.

In most works the precautions taken are sufficient for all ordinary purposes, and it is only when these are omitted on account of slackness, change of workers, etc., that troubles arise. The sudden development of cracked or warped saggars in a normal works is generally due to a change in the clay, so that this material should be the first subject of investigation. The various processes of manufacture should then be examined, as a broken screen or unduly worn blades in a pug-mill may cause much waste.

Mending Saggars.—Much may be done by carefully mending the saggars before the damage they have suffered has become too great. The mixture of clay and grog which is often used is by no means satisfactory, as the clay shrinks and the joint easily falls out. The " ideal " cement for this purpose is composed chiefly of grog (roughly ground broken saggars), to which a little water-glass has been added, the whole being worked into a stiff paste. The one drawback to this material is that it soon hardens and must, therefore, be made up as required. It may, however, be kept in an air-tight tin for some time, and this is the easiest method of preserving it. Some water-glass is too thick to work well; it should then be diluted with boiling water (it will not mix with cold water) until a pint of the mixture weighs 27 ounces. Should such a mixture prove too porous, it may be improved by the addition of a very small proportion of fireclay dust, which should be mixed with the grog before the water-glass is added. The proportion of each ingredient which gives the best results depends to some extent on the nature of the grog used. The following figures will do as a basis, but may require alteration to suit particular grog; grog 11 ounces, fireclay dust 5 ounces, water-glass 4 to 5 ounces. Instead of grog, carborundum firesand may be used; it has several advantages, but is somewhat expensive.

A properly mended saggar should be stronger than a new one so far as the mended portion is concerned; if this is not the case, the jointing has been badly done or an unsuitable mixture has been used. When using a cement containing water-glass, the fact must not be overlooked that this material requires a fairly high temperature to harden it properly and that the repaired saggars must be baked before they are used.

CARBORUNDUM SAGGARS.[1]

Carborundum appears to possess several advantages over the ordinary saggar mixtures, as it may be made up into saggars which have practically

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[1] The term *carborundum* is very widely used as another name for silicon carbide; strictly it should only be applied to the silicon carbide made by the Carborundum Co., Ltd.

no porosity and a very low coefficient of expansion, which renders them unlikely to crack on account of sudden changes of temperature, high refractoriness under load, and ability to bear a pressure of 50 lbs. per square inch at much higher temperatures than ordinary fireclay saggars. In addition, the strength of carborundum saggars is so high that they need only have one-fifth of the thickness of fireclay saggars for the same capacity, so that the saving in fuel which could, apparently, be effected by the use of carborundum is very considerable and well worth further consideration.

The chief drawbacks to the use of carborundum are: (i) its cost; (ii) its reducing effect upon any iron compounds used in the binding clay, which, if excessive, may cause "boiling" and contaminate the sand or flint used for placing the ware, and in some cases may discolour the contents of the saggar. H. Spurrier has also shown that the presence of iron in the carborundum causes the formation of iron carbonyl from reaction with the carbon monoxide in the kiln gases. The iron carbonyl is, later, decomposed into free iron and carbon, which discolours the ware. Carborundum freed from iron does not cause this discoloration; (iii) the liability of small cracks appearing the first time the saggar is burned, so that it has to be patched up before it can be used.

Some of these objections are lessened or even removed if the proportion of carborundum does not exceed 60 per cent. of the material. As little as 30 per cent. of carborundum will greatly increase the durability of saggars otherwise made of grog and fireclay and, on account of the high thermal conductivity of the carborundum, will save fuel.

These drawbacks are by no means prohibitive, and a pottery manufacturer who gradually replaces his present saggars by carborundum ones will probably effect a considerable saving. For further information on the properties of carborundum and the manufacture of articles from it see pp. 193 and 532.

KILN FITTINGS AND FURNITURE.

For burning porcelain, pottery, and electrical ware, a great variety of supports is needed: these are known by the general name of *kiln furniture.* The term includes slabs or bats, various kinds of supports for the slabs, props, thimbles, stilts, spurs, and other articles. They are required to have similar properties to saggars and may be made of similar materials. The smaller articles (thimbles, stilts, etc.) must be made of finely ground material.

The greater heat conductivity of silicon carbide has resulted in its extensive use for bats, slabs, and supports.

CHAPTER XI.

MUFFLES.

MUFFLES are permanent cases or boxes of refractory material which are built into a furnace or oven, and are used to heat goods out of contact with flame. They thus serve a similar purpose to saggars, but, being in the form of chambers, they are more convenient for some purposes.

When fixed in place ready for use, a muffle or muffle-kiln is, in fact, very much like the ordinary domestic oven. In both there is a source of heat (flaming fuel), goods to be heated out of contact with the flame and smoke, and an outer structure with an interior chamber (the muffle), in which the goods are placed so that they may be heated by the flames and hot gases passing between the inner and outer structures.

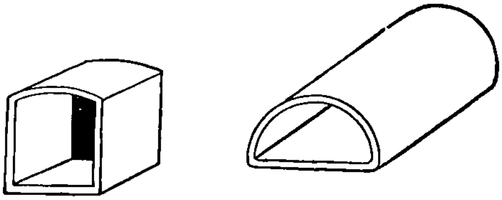

FIG. 120.—Muffles.

Muffles are chiefly rectangular in shape, but usually have an arched top (fig. 120). The front is open, but when the muffle is in use it may be closed temporarily by means of a refractory slab or by brickwork.

Muffles are of many different sizes, from a cross-section of 3 inches by 2 inches to 8 feet 6 inches by 9 feet, and the length may be anything between 8 inches and 30 feet. Small muffles are made in one piece, but larger ones are built of firebricks and slabs. Large muffles should usually be built in sections to allow for expansion and contraction; the joints between each section must overlap or be covered in such a manner that no flame or gases can pass through them.

The walls of a muffle should be as thin as possible consistent with the necessary strength, so as to permit the heat to penetrate them readily. They are seldom more than 4½ inches thick, even in the largest muffles, and ⅜ inch to ¾ inch in the smaller ones. The corners should be slightly rounded.

Some muffles have an opening in one side or at the top, to enable the man in charge to see into the interior whilst the muffle is in use. Such an opening may usually be kept closed, so as to retain the heat, but if desired, it may be left open so as to permit of the ventilation of the muffle. When substances are to be heated in a muffle in order to remove certain volatile matter, or when one of the results of heating the contents is a copious evolution of fumes, the use of one or more openings or " vents " is very desirable.

Uses.—Muffles are used in several industries: in metallurgy they are used for heating and annealing metallic bars and objects; in the manufacture of enamelled metal work they are used for fusing the enamel on the goods; in pottery manufacture they are used for fixing and developing the colour on decorative work and for burning large articles such as baths, lavatory basins, and other sanitary ware; in various other industries they are used for annealing and heating goods and materials out of contact with fire-gases.

Small muffles are specially useful in laboratories, for assaying, enamelling, hardening, and annealing small pieces of metal, and for experimental work. Small muffles made of *alundum* are particularly useful in furnaces heated by electricity. They can be used so often and have so high a degree of thermal conductivity that they prove cheaper than clay muffles, though far more costly to purchase.

The Materials.—Muffles are made of (*a*) fireclays, (*b*) grog and binding clay, (*c*) fused alumina (alundum, etc.), (*d*) silicon carbide (carborundum, etc.), or (*e*) silica. Electrically fused materials can be cast in the form of muffles, but these are not obtainable commercially.

Small muffles are usually made, in one piece, of (i) a mixture of fireclay and grog, (ii) silicon carbide with a ball clay bond, or (iii) fused silica.

Large muffles are usually built of bricks or slabs made of fireclay, grog, silicon carbide, or silica.

Silicon carbide has the great advantage of allowing much more heat to pass through it than do the other materials mentioned. It is also highly resistant to sudden changes in temperature and can be made very impermeable to gases.

Fused alumina has similar properties, but a lower thermal conductivity. It is much more resistant to oxidation.

Small muffles made of fused silica (see Chapter XV.) are highly refractory, will not crack with sudden and extreme changes in temperature, and effect a direct saving in time and fuel on account of the rapidity with which they may be heated. They have the further advantage of being quite impervious to furnace gases, so that contamination of the contents of the muffle by these gases is wholly avoided.

Muffles of fused silica are made in various sizes up to 28 inches by 16 inches by 7 inches.

Proportions.—The proportions of the materials used depend on the size of the muffle, the temperature to which it is to be heated, and the purpose for which it is to be used. Usually, the grading and proportioning of the materials is similar to those for firebricks (Chapter II.), saggars (Chapter X.), or glass pots (Chapter XIII.), though a rather larger proportion of grog is used when possible. Good mixtures for muffles contain 1 part of clay to 1 to 2 parts of grog. The larger the muffle, the coarser should be the grog, so as to give the necessary porosity and insensitiveness to sudden changes in temperature. A considerable improvement in the durability of muffles would be obtained if the materials used were more skilfully graded and if greater attention were paid to obtaining mixtures specially suited to the purpose. Most of the muffles now in use are made of too dense a material, which is necessarily very sensitive to frequent heating and cooling. Speaking generally, the more porous the material, the better it will be for the manufacture of muffles.

The slabs or bricks used for muffles of silicon carbide are made as described in Chapter VIII.

As lightness of construction and porosity are valuable features in a muffle, some makers use up to 25 per cent. of sawdust in the material of which the muffle is made. This addition is more useful in small muffles than in larger ones; the porosity of the latter is best obtained by the use of coarse grog or kieselguhr. The addition of *graphite* would also be advantageous for the reasons given on p. 586, but the author is aware of only one user of plumbago muffles, notwithstanding their advantages.

Muffles are subject to frequent changes in temperature, so that the proportion of grog and pore-forming matter used should be as large as possible in order to produce a porous mass, and the paste should be pugged thoroughly, and allowed to sour well, so that the smallest possible proportion of clay may be used.

Making.—Small muffles are usually made on a wooden core covered with wet calico and provided with a shoulder or thickness-piece at one end to enable the workmen to gauge the thickness of the muffle. The clay is batted out on another sheet of wet calico and wrapped around the core, as when making a saggar. The calico is then removed and the clay joined and trimmed. When the clay is partly dry, the core is removed and the drying is finished with the muffle standing on its closed end on a warm floor or rack.

Rather larger muffles are made either on or in a wooden mould, like retorts (Chapter XIV.), or in a press. Plaster moulds are occasionally used, but are generally considered to be too costly for renewals, as the plaster wears rapidly. Small muffles may also be made by casting, like glass pots (Chapter XIII.).

Large muffles are built of slabs, specially shaped blocks or bricks, usually with "tongues and grooves" to make tight joints.

The plates, slabs, or bricks used for larger muffles are made as described in Chapter IX.

Attempts have been made to produce muffles by expression from a pug-mill fitted with a die, the end being attached afterwards. By this method, however, it is extremely difficult to make the end with precisely the same shrinkage and density as the remainder of the muffle, with the result that it often falls away or cracks. It is not impossible that the use of a device similar to that employed for hollow blocks, with all the sides closed, may greatly facilitate the manufacture of muffles. So far, however, this has not been done.

The compression of muffles from a clot of clay placed in a die-box and subjected to the action of a plunger is exceedingly difficult on account of the shape and thinness of the walls of the muffle. This process is occasionally used and, if carefully supervised, is rapid and cheap where an enormous number of muffles of the same size are required. Special care is needed in fitting the closed end of the muffle on to the "pipe," or it will fall away when the muffle is heated.

Drying.—Muffles must be dried very slowly and carefully, as they are liable to twist and crack. The most convenient form of dryer consists of racks made of 1-inch pipes heated by steam. The muffles are placed on boards or steel pallets and the latter are laid directly on the pipes. This arrangement may be used to give a top heat as well as a bottom heat when desired.

Burning.—Small muffles are usually burned in muffle kilns and are usually piled on top of each other in columns. They may also be burned in down-draught kilns; this enables them to be burned at a higher temperature, which is advantageous.

Properties.—The properties which a muffle must possess are:

(i) *Resistance to the highest temperatures attained in use.*—This is not generally a matter of great difficulty, and ordinary refractory materials of good quality will usually suffice.

(ii) *Resistance to sudden changes in temperature*, as the doors are repeatedly opened in enamelling, and in some other uses of muffles, and a current of cold air may chill the muffle and crack it if it is made of unsuitable materials. Insensitiveness to sudden changes in temperature is usually increased by using a porous material, such as that formed by mixing sawdust with the clay used for making the muffle blocks or parts. The proportion of sawdust must not be excessive or the muffle will be too permeable to gases.

(iii) *Good thermal conductivity*, so that the heat may be transmitted rapidly to the interior of the muffle. The fireclay bricks usually employed for large muffles are not satisfactory in this respect, as they do not transmit heat readily. Fused alumina and silicon carbide slabs have a much higher thermal conductivity and are better, but more costly. By using muffles made of silicon carbide the rapidity of heat-transference is increased so greatly that one-quarter to one-third of the fuel may be saved; such muffles are also very resistant to sudden changes in temperature. This is especially the case if the muffle is built of thin slabs of silicon carbide. Silica is better than fireclay as regards conductivity, but unless fused silica (p. 698) is used in small muffles they will be too sensitive to sudden changes in temperature. The best that can be done with fireclay muffles is to make the walls as thin as possible, so that there may be a minimum of resistance to the passage of the heat.

(iv) *Impermeability* to flame and smoke and to harmful gases. There is seldom much difficulty with regard to this, unless an excessive amount of very coarse sawdust has been used, whereby such large pores have been formed that the muffle is not gas-tight. No muffle which has not been glazed internally is truly impervious to gases, but under ordinary conditions of use it is sufficiently impervious. Porous muffles are unsatisfactory for some over-glaze decorations and for other purposes where reducing gases are objectionable. In such cases an impermeable material, such as some form of silicon carbide, should be used and care should be taken to repair, at once, any leaky joints which may occur. Muffles capable of withstanding temperatures above 1600° C. have been prepared by D. Turner,[1] from a mixture of 20 per cent. of fused alumina and 80 per cent. of china clay, by casting. They should be fired at 1560° C. and afterwards glazed with a frit composed of china clay 40, quartz 30, and felspar 30 parts, mixed with 5 per cent. of china clay and applied by spraying. The glazed muffles are fired at 1600° C.

(v) The materials of which the muffle is made must not shrink when in use, or the muffle may crack and so fail in its work. To prevent this defect, the blocks, or slabs, of which the muffle is made will require to have been burned to a temperature somewhat higher than that at which the muffle is used.

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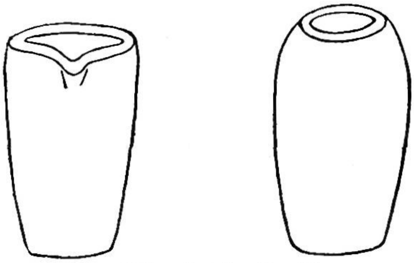
[1] *Trans. Faraday Soc.*, 1931, **27**, 113.

CHAPTER XII.

CRUCIBLES, SCORIFIERS, AND CUPELS.

Crucibles (figs. 121 and 122) are highly refractory, open-mouthed vessels which are used for heating various materials and particularly for melting metals, alloys, enamels, etc. The special crucibles used for making glass are described in Chapter XIII.



Figs. 121 and 122.—Crucibles.

Crucibles are of all sizes, from those, 1 inch high, which are used for testing, to the large crucibles used by steel-melters, which are 16 inches to 29 inches in height, about 9 inches in diameter at the widest part and 6 inches to 8 inches at the mouth. These large crucibles hold 70 to 75 lbs. of iron, cut into small pieces, but this amount, when melted, occupies little more than half the capacity of the vessel.

Scorifiers or *roasting dishes* (fig. 123) are a kind of shallow crucible and are made in a similar manner. They are used for exposing ores, etc., to air at a high temperature in order to effect the oxidation of one or more of the constituents. They require to have the same properties as crucibles.

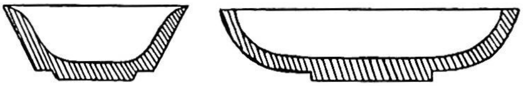


Fig. 123.—Scorifiers.

Cupels are small cylinders, usually weighing about half an ounce, the tops of which are slightly "dished" or hollowed. They are used in the refining and assay of gold and silver in order to separate these metals from copper, lead, and other metals which are more easily oxidised. Cupels are usually made of bone ash, as this material readily absorbs the oxides of lead, copper, etc., but is impervious to molten gold and silver, so that the latter remain on the cupel.

The bone ash should be as pure as possible, and should consist almost wholly of tri-calcium phosphate. It is moistened slightly with water, to which a little dextrin is sometimes added, and shaped in a small screw press. The cupels should be kept for a few weeks before being used, in order that they may be quite dry.

Crucible covers are made in a similar manner to the crucibles and of the same or less refractory materials.

Good crucibles and scorifiers are amongst the most difficult of any clay goods to manufacture, owing to the strains and conditions to which they are subjected. The processes of manufacture are easy, but the skill required in the selection of suitable materials and blending them in correct proportions and in a proper manner is much greater than is usually imagined.

In some cases, the contents of a crucible or scorifier may include an extremely complex mixture of fluxes, metals, and metallic oxides, and the problems involved by the actions of such a mixture are often of the greatest complexity imaginable. Different metallic oxides behave in ways which can only be learned by actual trial, and thus still further increase the difficulties. For instance, copper ores (usually sulphides) in the fluid state are very active when in contact with a body very high in alumina and much less active in contact with a highly siliceous body. On the other hand, lead ores scarcely attack a crucible high in alumina, but they will eat through a highly siliceous crucible in a very short time. Crucibles and scorifiers must, therefore, be made to resist the action of any substances which may be present.

Crucibles and scorifiers must have great refractoriness and a dense surface to resist the chemical action of the contents and the ash of the fuel used to heat them. They must also be entirely unaffected by very sudden changes in temperature, as they are taken out of the furnace and their hot contents emptied rapidly—a condition which is extremely trying to all refractory goods.

Crucibles may be classified according to the nature of the materials of which they are made or the purposes for which they are to be used. The following grouping is convenient:—

(*a*) Clay (or grog) crucibles.[1]
(*b*) Siliceous crucibles.
(*c*) Carbonaceous crucibles.
(*d*) Lime and magnesia crucibles.
(*e*) Alumina crucibles.
(*f*) Carbide crucibles.
(*g*) Porcelain crucibles.
(*h*) Crucibles of special materials.

Clay crucibles are very suitable for general work. They withstand the action of fluxes better than most other crucibles. They are made of grog and fireclay. Many crucibles manufactured in Great Britain are made of fireclay with about one-quarter of its weight of grog, but for some better-class work ball clay with a much larger percentage of grog is used. On the Continent, grog crucibles are usually made of a more siliceous clay than ball clay, but otherwise they have similar properties to the British crucibles.

Freiburg crucibles—which have long been famous for smelting processes in which a large amount of corrosive slag is formed and for assaying ores—are made of a mixture of 3 parts of fireclay and 1 part of grog. Many British crucibles have a similar composition, though some manufacturers prefer to substitute a Devonshire ball-clay for fireclay, and to use a larger proportion of grog.

London crucibles (fig. 124) are made to be specially resistant to fluxes, but they are very sensitive to sudden changes in temperature. The name is used more with reference to the shape than to the composition of the material or

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[1] Many so-called *clay* crucibles contain a large proportion of grog, and may equally well be termed *grog* crucibles.

place of manufacture. They are usually made of a mixture of fireclay, ball clay, and grog. One firm makes London crucibles of equal parts of clay and grog, but the usual proportions are those mentioned for Freiburg crucibles.

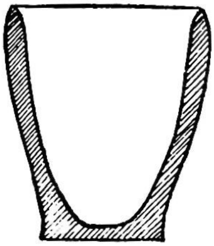

FIG. 124.—London crucible.[1]

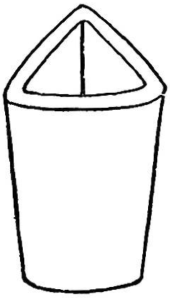

FIG. 125.—Hessian crucible.

Hessian crucibles, the fame of which for melting gold, silver, and other precious metals and in the chemical industry is known throughout the world, are of the siliceous type, and are made of Gross Almerode clay and Epterode sand, in the proportions of 2 : 4 to 5. This clay melts at Seger Cone 33 to 34 and has the following composition :—

Silica	64	per cent.
Alumina	24	,,
Iron oxide	2	,,
Lime	1	,,
Loss on ignition	7	,,
Other constituents	2	,,
	100	

Some of the Gross Almerode clay has a composition very similar to that of china clay, but with about 2 per cent. of iron oxide. This is only used for special crucibles.

Hessian crucibles (fig. 125) are somewhat triangular in shape, so that the molten contents may be poured out at any corner. In composition and general qualities they resemble Cornish crucibles, but are more fusible. Iron cannot be melted in them, as they are not sufficiently refractory.

For some years past the British trade in Hessian crucibles has been diminishing, as it is found that the corresponding crucibles made in this country have all the desirable properties of the Hessian ones for most purposes, coupled with the advantage of English manufacture.

Such crucibles are much cheaper than those made of plumbago or graphite, but are less suitable for general work, because they cannot be cooled without serious risk of damage, it being necessary to put them back in the furnace as soon as the contents have been poured out. Even when every care is taken, only two or three meltings in succession can be relied upon with clay crucibles. There are many operations where a crucible is only used once, and for these a clay crucible is often satisfactory, as it is sufficiently cheap to be thrown away, and all risk of contamination of the charge by material from a previous

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[1] To facilitate the separation of metals from supernatant slag some crucibles are provided with a partition such as in an arrangement patented by A. M. Clark in 1884.

one is avoided by using a fresh crucible each time. Unfortunately, clay crucibles, even when new, cannot always be relied upon and, if slightly damp, will break when heated rapidly. Yet in spite of all these drawbacks they fill a need in many industries and are extensively used.

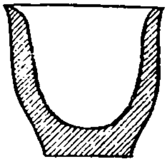
FIG. 126.—Cornish crucible.

French crucibles had at one time a high reputation for their refractoriness, combined with stability on sudden changes in temperature and resistance to fluxes, their peculiarly fine texture, and their porosity. They are made of highly plastic clay with twice its weight of grog and are usually lined with a lean, refractory clay. Some French crucibles are siliceous, like Hessian crucibles.

Cornish crucibles (fig. 126)—which are largely used in copper assaying and general experimental work—are also of the siliceous type and are usually made of—

Teignmouth ball clay	1 part.
Poole (Dorset) ball clay	1 ,,
St Agnes Beacon sand	2 parts.

(A little china clay is sometimes added.)

Cornish crucibles are usually 3½ inches high and 3 inches diameter; larger ones are very liable to crack.

Cornish crucibles are burned in kilns before being sold, and have the advantage that they may be placed in a hot furnace without cracking. They are not refractory enough for melting steel.

The most serious drawback to all clay crucibles which are free from plumbago or graphite is their sensitiveness to sudden changes of temperature. It is seldom possible to use such crucibles repeatedly, and some firms use them only once. Fortunately, they are cheap, and the use of a fresh crucible each time eliminates the contamination of the charge by a residue from a previous melt.

Siliceous crucibles are chiefly made of mixtures of sand or crushed silica rock and clay (see "Hessian," "French," and "Cornish Crucibles"), but some are made of fused silica.

Crucibles of crystalline silica, which are more refractory than those of fused quartz (*infra*), are made of water-ground quartzite previously burned at 1550° C. An organic bond such as cellulose acetate is added, and the crucibles are burned at 1500° C. before use.

Fused silica is an excellent material for the manufacture of crucibles up to 20 inches high by 12 inches diameter, as, being acid-proof and non-porous, they may be used for a large variety of work for which clay crucibles are unsuitable. They are specially suitable for melting metals which do not form basic oxides, and the smoothness of the silica and the absence of porosity enable the contents to be discharged in a particularly clean manner. Crucibles made of fused silica are also useful for many ignitions carried out in chemical laboratories and form an efficient substitute for those made of platinum. They are more constant in weight than crucibles made of porcelain, and may be heated and cooled with greater rapidity without injury. Crucibles made by the fusion of quartz are naturally glossy and transparent; those made of vitreosil have a semi-transparent appearance, but they can be glazed with a transparent coating of fused silica and are then as smooth as those made of porcelain. These glazed crucibles (like those of quartz) can be used repeatedly with aqua regia without loss of weight; they are also unaffected by the reducing flame of a gas-burner when used for igniting chemical precipitates.

Carbonaceous crucibles contain plumbago[1] (graphite), coke, or charcoal, in addition to the other ingredients. They are known by the generic name of *plumbago crucibles* or, occasionally, as *graphite crucibles*, and may readily be distinguished by their characteristic dark-grey colour. They are chiefly used for metallurgical purposes and in electrical furnaces.

The addition of carbon affords several important advantages: it increases the heat resistance, reduces the tendency of the contents to oxidise, enables heat to pass more readily into the interior of the crucible, and diminishes the sensitiveness of the crucible to sudden changes in temperature so much that plumbago crucibles may be subjected to very sudden changes without cracking and may be used repeatedly, so long as they remain sufficiently thick not to break.

Plumbago crucibles are chiefly made of a mixture of one or more clays, grog, and either graphite or coke. The clay and graphite form the chief constituents, the grog and free silica (if any) being added to keep the shrinkage within convenient limits.[2]

Many modern graphite crucibles on the Continent are made of graphite, *silicon carbide*, and clay, the two former being used on account of their high thermal conductivity, which reduces the fuel required to melt the contents of the crucibles. As early as 1918 Linbarger[3] found that if silicon carbide is added to the usual graphite and clay mixture, crucibles will stand sudden changes in temperature with much less risk of cracking.

A type of crucible largely in use at the present time consists of

Graphite	40–50 per cent.
Silicon carbide	10–20 ,,
Grog	0–5 ,,
Fireclay	30–40 ,,

For the manufacture of graphite or plumbago crucibles, whilst various clays may be used, there is none better than a plastic fireclay or a mixture of such fireclays. The clay must be plastic enough to retain the desired quantity of plumbago. Lean clays can only hold such a small proportion of plumbago that they are almost useless. According to Bleininger, clays most suitable for bonding with graphite should have a pore-ratio of 1·1 and a modulus of rupture, when mixed with an equal volume of sand, of 325 lbs. per square inch. The vitrification temperature should not be higher than 1150° C., but the clay should not be overfired at 1400° C. The refractoriness of the clay should be similar to that of Cones 31 to 33. China clay and sand are sometimes added to clay for steel-melting crucibles with noticeable increases in the refractoriness of the body. An excess of china clay should not be used, however, or the life of the crucible is unduly shortened. Ball clay may be very satisfactory for a portion of the china clay, but an excess of ball clay must be avoided.

Instead of clay, other bonds such as dextrin or treacle may be used, but are not satisfactory. E. Trutzer (Ger. Pat. 355,484), in 1920, patented the use of colloidal graphite as a bond (see *Carbon crucibles*).

[1] As a substitute for simple plumbago, P. F. Johnson, in 1894, patented the use of plumbago which has been soaked in a hot solution of alum, then mixed with steatite, evaporated to a stiff paste, and tempered. For the further use of steatite see p. 589 and Chapter XVI.

[2] The manufacture of crucibles from a mixture of 1 part of fireclay with 4 parts of a mixture containing 75 per cent. of plumbago and 25 per cent. of sand was patented in 1878 by G. W. Bantor.

[3] U.S. Pat. 1,277,227, 1918.

Other additions, besides graphite, may include sand or crushed silica rock, sillimanite, or silicon carbide. The last-named is sometimes used instead of grog on account of its greater thermal conductivity.

In crucibles with only a small proportion of carbon (2 to 6 per cent.), the latter is usually in the form of coke-dust. More than 10 per cent. of coke cannot usually be added, as it increases the shrinkage, makes the crucible porous and weak, and the coke burns away too readily. In the manufacture of steel, coke is less satisfactory than graphite, as it is less dense and dissolves more rapidly in the metal. Crucibles with a high proportion of carbon (either as graphite or coke) are not so satisfactory for melting high-grade steel and some other alloys as crucibles which contain little carbon. The carbon is dissolved by the metal or becomes mixed with it and often has a marked effect on its properties which may spoil it for some purposes. Moreover, crucibles rich in carbon are not tough enough at the temperature of molten steel and they are considered more dangerous to the workmen, as plumbago crucibles are liable to crush under the pressure of the tongs. Thus, in the manufacture of high-grade steels, the crucibles used contain only about one-twentieth of their weight of graphite or coke-dust, whilst for some other purposes as much as 50 per cent. of graphite may be present. A crucible rich in graphite will last longer and is, therefore, cheaper to use, but when a high-grade steel is to be produced a clay crucible with little or no graphite is the only one which will give entirely satisfactory results.

In a plumbago crucible, the graphite or coke is prevented from burning away by the thin film of glaze which is formed automatically by the ashes in the fuel used for heating the crucible. As it is important that the film should be formed rapidly, a little salt may be thrown on the fire, or a little felspar may be mixed with the materials of which the crucibles are made. The latter suggestion—though made by so eminent an authority as Seger—is not generally advisable; a wash over with water-glass is far preferable—see lining crucibles.

Carbon crucibles are made by turning gas-retort carbon (*retort scurf*) to shape in a lathe. They are occasionally used for high-temperature work, but are expensive. Such crucibles are also made by mixing finely ground graphite and tar, moulding under pressure and then burning at a dull red heat so as to cause the tar to coke and bind the particles of graphite together, or by using a mixture of purified lampblack and a chlorinated hydrocarbon as binder, as suggested by F. R. Daot. Colloidal graphite may sometimes be used as a bond for graphite crucibles. The colloidal graphite is prepared (i) by treating ordinary graphite with potassium permanganate, chromic acid, or other oxidant, and an aqueous solution of some colloid such as gelatin is added; the liquid is diluted, and the colloidal graphite formed is separated and washed with water; or (ii) the graphite is ground with water in the presence of tannic acid or other suitable dispersing agent.

The use of titanium silicate, oxide, and aluminate in graphite crucibles was patented in 1928 (Eng. Pat. 322,476). A typical mixture consists of graphite 30 to 60, silicon carbide 17, ball clay 30 to 45, and titanium dioxide 1 to 5 parts. The titanium compounds are supposed to prevent oxidation of the graphite and carbide.

Impregnated crucibles are made by filling the pores of the crucibles with a substance, such as coal-tar, which is decomposed on heating and leaves a residue of carbon (Eng. Pat. 278,367—1926). (See also p. 599.)

The impregnation of a mixture of graphite and clay with hydrocarbon gas was patented in 1923 (U.S.A. Pat. 1,503,150).

Lime crucibles are frequently made from a single lump of lime by soaking it in molten paraffin wax, tar, or resin, allowing it to cool and then turning it to shape on a lathe. The soaking is necessary to prevent the lime slaking and falling to powder before use. Larger crucibles of lime are usually made by coating the interior of a large fireclay crucible with lampblack and then tamping the powdered lime into it, a wooden core being used to form the interior of the lime crucible. The lampblack prevents the lime attacking the clay crucible when both are heated. Crucibles may also be made by pressing powdered lime in a powerful press, but the lime rapidly corrodes the metal.

Lime crucibles were first made in 1868, but were not successful on account of their reaction with carbon, their tendency to slag with either siliceous or aluminous material, to form calcium ferrate with iron or iron ores, and their general tendency and liability to disintegration.

The manufacture of crucibles from ground limestone or dolomite, the particles of which are bonded with magnesium chloride, was patented in 1879 by E. F. Althaus, but crucibles made in this manner have never been extensively used.

The pressing of crucibles from lime bonded with plumbago or coke and using a pressure of 40 tons per square inch was patented in 1879 by G. E. Dering.

Sillimanite crucibles are made of the same materials as sillimanite bricks; they are highly refractory and are specially suitable for melting glasses for optical and experimental purposes.

Magnesia crucibles have been used for many years for melting platinum and other refractory materials and in electric furnaces. They are made of the same materials as magnesia bricks (Chapter IV.), and in a similar manner.[1] If nearly pure magnesia is fired at 1600° C. to 1700° C., the magnesia crystallises without a binder and the interwoven crystals form a strong mass. Jensen has made crucibles of fused magnesia by crushing the fused material so as to pass through a 40-mesh screen and using 5 per cent. of hydrated magnesia as a bond, the moulded crucibles being dried and fired in an electric furnace at 1800° C. The crucibles thus made were said to be uniform in composition and texture and quite strong, had a very small shrinkage, and were also quite stable at a temperature of 1900° C. Pure magnesia is not suitable for crucibles unless they have been burned at a temperature above 1550° C.; those burned at lower temperatures crack seriously when in use. The presence of a small quantity of alumina or of alumina and silica enables *spinels* (p. 235) to be formed, and crucibles made of such material are much more resistant to changes in temperature.

Small magnesia crucibles are best made of sintered or fused magnesia, with 2 to 5 per cent. of magnesium hydroxide or magnesium chloride as a binder, an organic binder, such as dextrin, being also used if desired. The particles of magnesia should pass through a 60-mesh, and at least 25 per cent. through a 200-mesh; if coarser particles are used the crucible may not be impervious. Of this fine material nearly half should be in particles less than 0 0016 inch and about 12 per cent. less than 0·0002 inch diameter.

[1] The following mixtures have been patented: F. M. Lyte, in 1885, patented the use of a mixture of dead-burned magnesia with 6 to 10 per cent. of magnesium hydrate or 15 per cent. of lightly burned magnesia. The use of magnesia bonded with boric acid was patented in 1897 by J. L. Dobell, and by Rawson & Littlefield in 1900. The use of a mixture of anhydrous boric and phosphoric acids as a bond was patented by Gebr. Siemens in 1910. H. Goldschmidt, in 1905, patented the use of magnesia bonded with water-glass for crucibles to be used in the thermit process, where the temperature attained is stated to be over 2000° C., though, according to O. Ruff, magnesia is too volatile for use above 2000° C.

The crucibles may be shaped in four ways:

(*a*) By using a plumbago or graphite crucible as a mould in which the magnesia can be burned to 1200° to 1400° C. It can then be removed and re-burned at any desired temperature.

(*b*) By packing particles of fused magnesia in a graphite mould [1] provided with a core and using a vibrating table to assist consolidation. The mould with the crucible is placed in a red-hot furnace and baked at 1700° C. The shrinkage is about 0·05 inch per inch diameter, so that the crucible is easily removed from the mould.[2]

Magnesia crucibles volatilise readily when heated in contact with carbon to 2000° C.

(*c*) By tamping the moist powder in a mould, in which it is afterwards burned.

(*d*) In a press under a pressure of 1500 lbs. per square inch, the die being lubricated with oil or water; or, preferably, the refractory powder may be moistened with dilute hydrochloric acid, but in that case the die must be cleaned after each batch of crucibles, or the acid will rust it.

(*e*) By fusing a mixture of magnesia and bauxite (see " Spinel," p. 235) in an electric furnace and casting the molten liquid in sand moulds.

Instead of making crucibles which are heated externally and must, therefore, have relatively thin walls, a similar result may be obtained by using electric induction furnaces, in which the walls of the container may be of any desired thickness. Such furnaces are not, strictly, crucibles, though used for the same purposes.

Magnesia crucibles should be burned at the highest practicable temperature. Small ones may be burned at 1900° C. in an Arsem or similar furnace. At this high temperature a felted mass of periclase crystals (p. 476) is formed and the quality of the crucibles is greatly improved.

Magnesia crucibles should be dense and impervious. They are not attacked by basic slags and are the most resistant of all types to lead oxide. If properly made so as to have no appreciable shrinkage when in use, they can be employed at all temperatures up to 2000° C. and for short periods up to 2500° C., provided the conditions are oxidising. Under reducing conditions and in contact with carbon, the magnesia is reduced to the metal, which rapidly volatilises, especially under reduced pressure.

Small magnesia crucibles fired at 1900° C. or above have a metallic ring and are quite strong mechanically. If adequately burned, the pores are completely sealed and the crucibles are impervious to air under a pressure of 200 mm. of mercury. The true specific gravity is 3·35 to 3·55.

The foregoing statements only apply to crucibles made of almost pure magnesia. Any appreciable proportion of impurities—especially iron oxide and silica—greatly reduces the temperature at which such crucibles can safely be used.

Crucibles made of *asbestos*, *lava*, *talc*, or *steatite* contain one of these materials mixed with fireclay, magnesia, or graphite, and sufficient water-glass to form a workable paste. Such crucibles are not highly refractory, but are often used for fusing caustic alkalies and other highly corrosive materials.

The use of steatite for this purpose was patented by J. H. Thorp in 1878, that of a mixture of fireclay and steatite by Hutton and Granger in 1883, and of steatite bonded with clay, coal-tar, or lime by A. F. Tigerstedt in 1900. The proportions of clay and steatite must be found by trial.

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[1] The mould and core are best made by machining them out of carbon electrodes.

[2] *Ind. Eng. Chem., Anal. Ed.*, 1937, **57**, 833–838.

In 1903, S. L. Mershon patented the manufacture of crucibles from talc heated in successive stages.

The manufacture of crucibles from *asbestos* bonded with water-glass was patented in 1877 by A. Dudgeon.

The use of the following mixture for this purpose was patented by A. Moszczenski in 1887: Fireclay 30 parts, glass 20, blast-furnace slag 20, sulphur 5, and asbestos 25 parts.

Harvard has recommended the following mixtures as excellent for asbestos crucibles:—

	I.	II.
Asbestos	25	25
Fireclay	37	37
Quartz	5	3
Graphite	17	32
Grog	16	..
Magnesia	..	3

The use of *barium sulphate* as the chief constituent of crucibles was patented by W. L. Wise in 1885.

Alumina crucibles are of four kinds:

(*a*) Those made of calcined bauxite, diaspore or other form of alumina, with a suitable binder.

(*b*) Those made of sintered alumina (sinter-corundum), which may be regarded as being intermediate in its properties between calcined bauxite and fused alumina.

(*c*) Those made of fused alumina (alundum, corundum, etc.).

(*d*) Those made of mixtures of several substances, the chief ingredient being one of the forms of alumina just mentioned.

Bauxite crucibles are usually made of a mixture containing calcined diaspore or bauxite and a refractory clay similar to that used for bricks. The proportions recommended in I. Werlein's (1911) patent are: 80 to 95 parts of alumina, 5 to 24 parts of silica, a little titanic acid, and beryllia or zirconia, the crucible being moulded, dried, and then burned at 2800° C. to 3000° C. in an electric furnace. The mixture of magnesia and alumina (*spinel*) described on p. 469 may also be used. C. Caspar (Eng. Pat. 69 of 1908) patented the use of pure amorphous alumina and a siliceous binding clay. St. Laurent and the Aluminium Solder Co. patented, in 1915, the use of a mixture of 70 parts of alumina and 20 parts of carbon, preferably charcoal, for the manufacture of crucibles. J. C. Waterhouse (1883) patented the use of a mixture of an aluminous fireclay, plumbago, asbestos, and small proportions of magnesia and quartz moistened with a solution of sodium silicate.

Alumina crucibles may also be made of (i) a mixture of gelatinous and calcined alumina,[1] (ii) alumina made by gently heating ammonia alum to redness, (iii) a mixture of gelatinous alumina, calcined alumina, and a product formed by heating equal parts of alumina and whiting until fusion occurs.

Sintered alumina (sinter-corundum) *crucibles* are made of alumina which has been sintered but not fully fused.

A French patent, granted to N. Lecesne in 1914, describes a novel method of making crucibles and other articles from fused alumina prepared as described on p. 208. The crushed material is washed, treated with magnets to remove the iron, and is then mixed with water, ground flint, and a little

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[1] Deville used this mixture in 1856 and, later, one composed of equal parts of alumina and marble. Bauxite appears to have first been used for crucibles in 1869.

quicklime. The resultant paste is pressed in powerful presses to the required shape, and the articles are burned in ordinary kilns at a temperature of about 1400° C.

Crucibles made of sinter-corundum are usually produced by slip-casting (p. 611) from a slightly acid suspension, but some are made by mixing the powdered material with an organic binder such as dextrin and then pressing. Their properties are almost identical with those of fused alumina crucibles, but the latter are slightly superior owing to the absence of impurities and the greater development of crystalline alumina.

Crucibles of *fused alumina* may be made by melting alumina in an electric furnace and casting it into moulds made of refractory sand in a manner similar to that used for making iron castings. The crucibles are produced upside down and are somewhat rough.

A. Malinovsky [1] was one of the first to produce a molten magma of refractory material other than silica, but G. S. Fulcher [2] was responsible for the development of fusion-cast material by means of an electric arc. Considerable improvements have been made since 1935,[3] and crucibles made by the Thermal Syndicate, Ltd., Wallsend-on-Tyne, are accurate in shape and of ample smoothness for most purposes.

Similar crucibles may also be made by mixing the fused alumina (alundum) with dextrin or other agglutinant and heating to partial fusion in an electric furnace; the heating must be somewhat rapid or the material falls to pieces. Where extremely refractory crucibles of an aluminous nature are required, these alundum crucibles have proved quite satisfactory, though they are too costly for general use. They will withstand any temperature available in the laboratory, and this, together with high thermal conductivity, makes them especially valuable for coal analyses, drying materials, igniting filters, and other general use on a large scale, but are excellent for laboratory and small-scale work, *e.g.* for melting rare metals and special alloys of high melting-point.

Crucibles made of fused or sintered alumina are more sensitive to sudden changes in temperature than are crucibles made of fused silica; this sensitiveness is reduced by using a mixture of china clay and alumina instead of fused alumina alone, but the refractoriness is also reduced slightly.

Crucibles of pure fused alumina can be used at a working temperature of 1950° C., and those containing china clay at about 1700° to 1800° C. according to the proportion of clay present. Some volatilisation occurs at 1350° C. and at 1470° C.; a change in the crystalline form, with an alteration in the volume, may occur and limit the use of the crucibles at and above that temperature.

Such crucibles and those made of sinter-corundum contain up to 99·8 per cent. of alumina with only traces of impurities. They are not affected by boiling caustic soda, which seriously corrodes porcelain, nor by fused sodium chloride or sulphate, but are very slightly attacked by alkali fluorides, alkali carbonates, and lead compounds.

Crucibles made of sinter-corundum are the most resistant of all ceramic crucibles. They are also highly resistant to hydrofluoric acid and to phosphoric acid, to steam and to slags.

At high temperatures, such crucibles have a greater resistance to attack than any other pure oxide, and do not form a carbide like thoria, magnesia, beryllia, and zirconia.[4]

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[1] *J. Amer. Cer. Soc.*, 1920, **3**, 40.

[2] U.S.A. Pats. 1,615,750 and 1,615,751.

[3] See Partridge and Lait, *J. Soc. Glass Tech.*, 1936, **20**, 201.

[4] Partridge and Lait, *J. Soc. Glass Tech.*, 1936, **20**, 214.

Crucibles made of pure alumina are usually very porous unless burned at very high temperatures. The porosity can be reduced: (i) by varying the composition and using a larger proportion of fine material; (ii) by soaking in a solution of aluminium chloride, drying and refiring, this being repeated as often as necessary; or (iii) the outer surface can be fused with an oxy-hydrogen flame.

When crucibles or other articles made of alumina have been burned for a long time at 1900° to 2000° C., a recrystallisation of the alumina occurs and an extremely hard, translucent body is formed which is highly resistant to corrosion and has a low permeability. The term "crystalline alumina" should not be applied to bricks or other articles which contain less than 80 per cent. of definitely crystalline alumina.

Carbide crucibles[1] consist chiefly of silicon carbide which has been mixed with clay or other suitable bond (see "Carborundum Bricks," p. 532). The use of glue as a temporary bond was patented in 1920 by F. A. Fitzgerald, and of lime by G. A. Baly. The use of graphite as an ingredient was patented in 1920 (Eng. Pat. 176,436), and the production of a carbide *in situ* by making crucibles of a mixture of graphite and silicon was patented in 1930 (Eng. Pat. 348,149).

Carbide crucibles are usually made in presses and are dried and burned like clay crucibles.

The chief advantages of carbide crucibles are: (*a*) the readiness with which heat passes through them, so that a saving of 25 per cent. or more fuel can be effected by their use; (*b*) they are so insensitive to sudden changes in temperature that they can be placed in or removed from the hottest furnace without any preliminary heating or annealing, and yet will not crack, spall, or flake. They must not be used for the few metals and alloys which attack them, but for most metals their use is rapidly increasing.

Chromite crucibles may be made of a mixture of chromite and ferro-silicon with a sodium silicate bond (Eng. Pat. 189,692—1922), or of a mixture of crushed chrome bricks and magnesite (Eng. Pat. 219,423—1923; U.S.A. Pat. 1,743,803). They appear to find very little use, and if chromite is an essential ingredient, better crucibles could be made in a manner similar to chrome spinel bricks (p. 529).

Porcelain crucibles are made in the same manner as hard-paste porcelain (see "Berlin Porcelain," p. 713).

Crucibles of special materials, in order to have a more than ordinary resistance to corrosion at high temperatures, must be made of *pure oxides*—usually without any permanent bond, though for some purposes a permanent bond may be used. The tendency of any permanent bond is to reduce the durability of the crucible, so that for the most stringent conditions no such bond should be used.

The materials used for such crucibles are pure refractory oxides which have been pre-heated to a temperature higher than that at which the crucibles will be used, so as to eliminate objectionable shrinkage, and, where practicable, the fused oxides are preferable. Such crucibles are chiefly used for melting carbon-free metals and alloys, glasses and various experimental mixtures of pure materials.

The most important of the " pure oxides " used for crucibles are *alumina*, *magnesia*, *zirconia*, *thoria*, *titania*, *beryllia*, and the *spinels*. Mixtures of two

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[1] Commonly known as *carborundum* crucibles, though this is the proprietary name of articles made only by one firm and is not of general application. Carborundum crucibles are the subjects of Eng. Pats. 176,436 (1920), 176,437 (1920), and 207,677 (1922).

or more oxides may also be used if they are not incompatible ; thus alumina and titania (Eng. Pats. 322,476 ; 326,229), magnesia and alumina (see Spinels), zirconia and alumina, yttria, thoria, or magnesia have all been used for crucibles (see p. 712).

Pure alumina is obtainable as a commercial product containing more than 99 per cent. of alumina. It should be sintered or fused in an electric arc (see p. 590).

Pure magnesia is obtainable commercially, but prior to using it for crucibles it should be sintered or dead-burned—preferably in an electric arc (p. 219).

Pure zirconia is obtainable commercially as an almost pure oxide, and must be heated intensely (preferably in an electric arc) before being used for crucibles.

The best zirconia crucibles[1] are made without any added bond, the finest particles of zirconia (colloidal zirconia—see p. 495) or a salt of zirconia (such as zirconium chloride, added as such or formed by adding a little hydrochloric acid to the zirconia)[2] cementing the coarser particles together.

Crucibles made of pure zirconia are usually too porous, but the addition of 1 to 3 per cent. of calcined thoria or fused magnesia reduces the porosity to about 2 per cent. without lessening the refractoriness. The addition of 10 per cent. of fireclay also reduces the porosity, but it simultaneously lessens the refractoriness and makes the ware soft and inclined to blister. The same objection applies to mixtures of zirconia, graphite, and fireclay. For further information on the use of mixed oxides see p. 594.

Zirconia crucibles should not contain much silica, as this reduces the refractoriness. Many of the "zirconia crucibles" sold a few years ago could not be used above 1700° C. for this reason, whilst those of the best quality may be used up to 2200° C.

The use of a mixture of equal parts of zirconia and carborundum was patented by W. R. Just in 1916. These substances appear to react and shrink, and the crucibles appear to have acquired a glaze.

Crucibles of pure zirconia are porous, crack very readily, and are uncertain in use ; they are much more reliable if made of 95 per cent. of highly calcined or fused zirconia, 5 per cent. of finely ground zirconia, 5 per cent. of aluminium chloride, and 5 per cent. of dextrin as binders. The cracking may also be eliminated by adding a small proportion of magnesia or yttria (see pp. 494, 495), because these prevent the inversion of monoclinic zirconia into the tetragonal form.

If sufficient care is taken in grading the material, fairly good crucibles can be made of 70 per cent. of fused zirconia crushed to 60-mesh, 15 per cent. of fused zirconia ground to 300-mesh, and 15 per cent. of refined milled (colloidal) zircon as binder (see p. 495), with a little dextrin solution for moistening, but even this material is easier to mould and cracks less readily if 10 per cent. of magnesia is added, instead of pure zirconia being used.

Ruff and Ebert[3] found that non-porous and non-cracking zirconia ware can be made by adding very small quantities of other oxides, and burning it in an exhausted carbon-tube resistance-furnace in a reducing atmosphere. They consider the best additions to be 1 per cent. of alumina for crucibles burned at 2000° C., 1 per cent. of thoria for crucibles burned at 2200° C., and 1 to 3 per cent. of yttria for crucibles burned at 2400° C. They found that beryllia, magnesia, and silica are all unsuitable for use in making zirconia

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[1] U.S.A. Pats. 1,615,750 and 1,615,751.

[2] Eng. Pat. 292,529 (1927).

[3] *Zts. anorg. Chem.*, 1929, **180**, 19–41.

crucibles, and that larger proportions of alumina, thoria, and yttria than those mentioned increase the porosity. Without some such addition, it is extremely difficult to produce zirconia crucibles which are not too porous and do not crack too readily.

Zirconia crucibles are highly resistant to slags and fluxes, but they have a low thermal conductivity, so that their contents " heat very slowly." For other properties see pp. 239, 497, and 595.

Thoria crucibles are made chiefly of the purest commercial thorium oxide; it may require to be freed from ammonium sulphate, but usually requires no other treatment than to be fused, allowed to cool, reheated to about 1000° C., then quenched in cold water and ground to a fine powder.

The most refractory crucibles are made without any admixture (other than a bond), but several patents have been granted for mixtures of thoria with other substances (see *below*). The use of a mixture of calcined and raw thoria was patented in 1926 (Eng. Pat. 280,907) and the use of a mixture of thoria 40, thoria grog 20, colloidal thoria 5, and an electrolyte 2 parts was patented in 1924 (U.S.A. Pat. 1,512,801; other English Patents are 11,771—1912, 3118—1913, 21,378—1914, 2438—1915, and 189,492—1921).

Crucibles made of pure (fused) thoria have been used satisfactorily at 2200° C.

Thoria crucibles of good quality may be made of ground fused thoria bonded with a solution of thorium chloride and fired at 1600° C. in an electric (induction) furnace. Alternatively a bond of colloidal thoria may be used.

T. Terrell and Monarch Maulles, Ltd., have patented (Eng. Pat. 189,492) a mixture of thoria and thorium nitrate with small quantities of other oxides and salts for crucibles.

Beryllia crucibles are important because beryllium oxide can be used at 2300° C. without reduction by carbon. They are best made of pure beryllia with finely milled (colloidal) beryllia as a bond, but various mixtures of beryllia with other oxides have been used (see mixed oxides, *below*).

Beryllia crucibles are made in the same way as thoria crucibles, and many of the same patents are applicable. They are increasingly used in induction furnaces, as their resistance to reducing agents is greater than that of alumina, but metallic oxides (except zirconia) form low-melting slags with beryllium oxide at very high temperatures.

Beryllia crucibles (if made of fused beryllia) can be made perfectly gas-tight; they are good heat-conductors and insensible to very sharp changes of temperature. For this reason the use of beryllia crucibles in high-frequency furnaces is particularly successful. Caustic alkalies melted by direct flame do not affect such vessels as they do those of alumina, though beryllia crucibles are very susceptible to acids. The chemical resistance to reducing agents is higher than that of alumina, so that common metals and alloys with high melting-points, zirconium metal and beryllium itself can be melted without any risk of causing damage to the crucible; on the other hand, oxides such as alumina, magnesia, etc., readily form fusible slags with beryllia at high temperatures, though zirconia and beryllia can be left in contact up to about 1900° C. without causing the formation of slag. Even at very high temperatures carbon hardly affects beryllia.

Titania crucibles are unusual. O. Ruff[1] has made crucibles of titanium carbide with other carbides.

Spinel crucibles are made of the same materials as spinel bricks (p. 508).

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[1] *Forschungsarbeiten Gebiete des Ingenieurwesens*, 1914, p. 147.

Crucibles of mixed oxides are usually made of two or more of the following: alumina, magnesia, zirconia, thoria, titania, and yttria.

For many years the Elektrizitäts Gesellschaft have supplied crucibles of pure zirconia with 5 to 15 per cent. of yttria and also of zirconia with 4 per cent. of soda and ½ per cent. of magnesia.

Mixtures of zirconia and alumina (corundum) have also been employed.

Ruff and Lauschke have recommended a mixture of zirconia and magnesia, with starch and borax as bonds. They found that the use of a suitable proportion of water is important in facilitating the distribution of pressure and in preventing cracking when the crucibles are used.

Several experimenters have found that zirconia mixed with 3 per cent. of thoria or yttria and 1 per cent. of starch is satisfactory, but that a larger proportion of the added oxide is undesirable. Knofler & Co., in 1915, patented the use of a mixture of zirconia, titania, beryllia, and thoria with 1 per cent. of the colloidal hydrate of one or more of these substances and 0·1 per cent. of free acid.

Ruff and Ebert insist (p. 593) that only very small percentages of these oxides should be added to zirconia, as larger ones are detrimental.

The use of a mixture of magnesia and beryllium oxide was patented in 1933 (Eng. Pat. 434,092).

The use of a mixture of thoria and ceria was patented in 1921 (Eng. Pat. 189,492).

The use of a mixture of zirconia with sillimanite or with chromite has been attempted, but no results appear to have been published.

Zircon crucibles are made of zirconium silicate (p. 240). They are usually of poorer quality than those of zirconia. The best results are obtained with a mixture of 70 per cent. of granular refined zircon, 30 per cent. of finely ground (100-mesh) zircon and dextrin as a binder. The firing temperature must be about 1730° C.

Zircon crucibles are highly refractory, but do not withstand fluxes and slags as well as clay crucibles. Their porosity is reduced if a little magnesia is added to the zircon and the crucibles are burned at 2200° C. on a bed of zirconia.

Materials.—The various materials used for making crucibles have been mentioned on p. 583 *et seq.*, and further information on them is given in Chapter I. More specific information in relation to the use of these materials for crucibles (as distinct from other uses) is collected on this and following pages.

Clays.—The selection of clays for crucible manufacture requires great care. The principal requirements of such clays are: (1) great strength, as a crucible full of molten metal may weigh a hundredweight; (2) great resistance to sudden changes of temperature, as the crucible with its contents is brought suddenly from a temperature of perhaps 1500° C. to about 150° C., when it is taken from the furnace and its contents poured into moulds; and (3) a powerful reducing action to prevent the material becoming oxidised. This is secured by mixing carbon in the form of coke, graphite, or plumbago with the clay. Some crucibles also require special properties; for instance, crucibles for melting "Monel" metal require to be very smooth and impervious in order to secure a pure alloy.

These characteristics cannot be obtained by the use of a single clay, but must be obtained by mixing various materials together, the proportion of each, together with the amount of water used, determining to a large extent the properties of the crucibles.

For melting brass, the binding clays used should have a high crushing strength at about 1250° C., which is the maximum temperature attained by the brass. For steel-melting crucibles the clay requires to be more refractory, and should be dense and of a high crushing strength at 1400° C. to 1600° C.

As crucibles must generally withstand frequent and sudden changes of temperature, the clays used in their manufacture must have a high binding power, so that they may unite with as large a proportion as possible of non-plastic materials. This binding clay must not shrink unduly when heated, so that the limits of plasticity are comparatively narrow. It need not be highly refractory—though this is an advantage—but, whilst it is desirable that the clay should sinter (vitrify) at a moderately low temperature (Seger Cone 1*a* to 3*a*), it must retain its shape until a much higher temperature (Seger Cone 32 or above) is reached; in other words, it should have a long range of vitrification. It should, when fused, produce a viscous lava-like mass, as clays which fuse to a thin fluid are not suitable for crucibles. It must also produce a material of great mechanical strength (both tensile and crushing) when burned. The fractured surface of the burned mixture of grog and clay must not be too glossy or unduly dense, or it will not be able to stand sudden cooling. For further particulars see Chapter I., pp. 102 to 137.

It is almost impossible to find any one clay which is suitable for the manufacture of crucibles for some purposes, and it is, therefore, necessary to use several clays. Thus, for the manufacture of certain high-class steels it is customary to use four clays, all of a highly refractory nature, and of somewhat similar composition, because it is found in actual work that such a mixture is more durable than when one or two clays only are used. The composition of these clays is shown in the following table:—

TABLE LXXXIX.—COMPOSITION OF CRUCIBLE CLAYS.

	English China Clay.	Stourbridge Clay.	Derby Clay.	Stannington Clay.
Silica	46·3	63·3	52·0	47·6
Alumina . . .	39·9	23·3	36·0	25·4
Iron oxide . . .	0·3	1·8	1·8	3·5
Lime	0·4	0·5	0·8	1·0
Magnesia . . .	0·4	..	0·5	1·1
Combined water, etc. .	12·7	11·1	8·9	21·4

The clays used for making this kind of crucible are of two types—"white clay" or china clay, and "fireclay." Some makers distinguish a third or "local" clay, which is usually a bastard fireclay obtained in the district in which the crucibles are made. It is a curious fact that personal prejudices play so important a part in the manufacture, that more than one firm is buying clay and transporting it over a distance of forty miles or more, when the same geological bed runs close to their own works and the clay from the latter can be obtained at a nominal cost!

The *china clay* ("white clay") is purchased from Cornwall and is of the usual commercial quality.

The *fireclay*, of which two varieties are usually purchased from a distance, is generally obtained from Stourbridge,[1] Church Gresley, Swadlincote, Woodville, near Burton-on-Trent, and from Derby respectively.[2]

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[1] One of the earliest patents relating to clay crucibles is that of W. White, who, in 1762, specified a mixture of Stourbridge and Dorset clay with Woolwich sand and water for the manufacture of crucibles.

[2] With the exception of the first-named, clay from all these localities is often known s "Derby clay."

Stourbridge clay has a great refractoriness and fineness, but is low in alumina. The Derby fireclay, on the contrary, is rich in alumina and highly plastic (for a fireclay), so that it serves to increase the average alumina content, to bind the less plastic particles, and to give strength to the crucible.

The " local clay " is usually a typical fireclay of the Coal Measures, which crops out near the surface. It is relatively cheap, often contains an excessive proportion of alkalies, and is chiefly used as the result of the crucible maker's endeavour to experiment on his own account. Some works are particularly fortunate in this respect, *e.g.* the Black bed " Stannington " or " pot clay," which forms the lowest bed of the Yorkshire Coal Measures and lies directly on the Millstone Grit, is found in the neighbourhood of Sheffield and is much prized by steel makers. It is unusually rich in combined water, but is high in alumina for clays of this type, and is consequently very refractory, whilst at the same time its plasticity, when well weathered, gives it additional value. This clay is more fully described in Chapter I.

The value and suitability of a clay for the manufacture of crucibles depend upon its refractoriness under the conditions in which it will be used, so that the size of the particles and the method of preparation are often of more importance than the chemical composition of the clay. The selection of clays for the manufacture of crucibles must, therefore, be made with a knowledge of the purposes for which the crucibles are to be used.

It is of the greatest importance that clays used for the manufacture of crucibles should be properly *weathered.* There are few more foolish attempts at economy than those which seek to avoid the expense of weathering and souring the clay, or to subjecting it to some equivalent treatment.

Good crucible clays are rather rare, particularly where they are required for graphite crucibles. All good crucible clays are fireclays, but not all fireclays can be used for crucibles.

Bonds for crucibles are of two kinds:

(*a*) *Temporary bonds* such as starch, flour, tar, linseed oil, and cellulose derivatives such as sulphite lye and cellulose acetate. These burn away when the crucible is heated.

Linseed oil is sometimes used instead of water in making crucibles. It reduces the shrinkage which would occur with water and produces a very smooth paste which flows readily in the mould.

(*b*) *Permanent bonds* such as clay, sodium silicate and other silicates. They are useful for crucibles not subjected to the highest temperatures; in the most refractory crucibles (of pure oxides) they introduce too much impurity to be satisfactory. Fireclay is the chief clay used as a bond, but ball clays are sometimes preferable. When a clay bond is used, a plastic clay is essential; it must be sufficiently refractory but not excessively so, and it must not shrink unduly. The most suitable binding clays are dense when burned but not unduly vitrified. In England, the *ball clays* (p. 43) are chiefly employed for this purpose and if well selected are quite satisfactory.

An excess of binding clay should be avoided, as it tends to cause spalling and cracking.

The best bonds for pure oxides or mixed oxides are usually the hydroxides, chlorides or nitrates of the same elements; thus aluminium hydroxide is used with alumina, magnesium hydroxide with magnesia, and so on. These substances must consist of extremely small particles—preferably in or near the colloidal state.

Grog.—Various " additions," known as " grog," are used—chiefly to contro the shrinkage or to prevent cracking or undue corrosion by slags or fluxes. These additions should usually be in the form of rather coarse particles.

Silica, used in the form of crushed silica or white sand in some clay or graphite crucibles, is added to reduce shrinkage; some manufacturers have grave doubts as to its value (but see " Hessian Crucibles," p. 584). If a highly siliceous clay is used the proportion of sand is reduced or the sand may be omitted.

The *grog* should be clean and well graded. Some crucible manufacturers prefer grog made from old crucibles, but if this is used allowance must be made for the graphite present, or the greater part of it should be removed, as described on p. 190.

Felspar is an ingredient in some crucibles used for brass melting, in order to increase the density of the crucible at a moderate temperature (1300° C. to 1350° C.), and thus lessen the cost of burning the crucibles as well as prevent waste of metal by absorption.

Free silica or *quartz* is sometimes added to crucible mixtures so as to render them less sensitive to sudden changes in temperature, but they are more readily attacked by fluxes and slags.

If sand or crushed silica is used, it should be of the same nature and have the same properties as that used for silica bricks. It is interesting to note, however, that in 1899 Pilkington and Ormandy patented the use of waste sand from glass works, this being moulded into crucibles and heated until the contained glass melts sufficiently to unite the sand particles into a hard mass on cooling.

Another interesting use of silica is that suggested by I. Schlossberg, who, in 1913, patented the admixture of about 93 per cent. of quartzite with 2 per cent. of colloidal silica and 4½ per cent. of lime, in order to form crucibles which are acid-proof as well as refractory. The crucibles are not burned, but are hardened by steam, and lime is eliminated by subsequently treating the crucibles with silico-fluoric or hydrochloric acid, followed by washing.

Glass and fireclay in equal parts made into crucibles which are burned at Cone 3 to 4 give a hard, vitreous, porcelain-like ware which is highly resistant to sudden changes of temperature and to abrasion and has great strength.

Carbon is usually employed in the form of *plumbago* (*graphite*) or *coke*, the former being used when a large proportion and the latter when a small proportion of carbon is required. In all cases, the graphite or coke must be crushed to a fine powder before use. The value and durability of plumbago crucibles depend largely on the purity of the graphite used; if this contains much mineral matter (ash) the crucibles will not be satisfactory.

The graphite for plumbago crucibles should contain at least 85 per cent. or more of carbon, and it must be free from mica, pyrite, and iron oxide. The grains or flakes should be coarse enough for them to be easily bound together by clay or other bond employed; the whole of the graphite should remain on a 100-mesh sieve, and should contain a large proportion of flakes about $\frac{1}{25}$ inch diameter. Ceylon graphite is particularly suitable for crucibles, as the grains are more cubical than the thin plates of graphite from other sources. An excess of flake graphite is undesirable, as it is " slippery," tends to adhere to the tool, and slide rather than pack against the mould, and does not unite properly with the clay and, therefore, causes lamination, which is a very troublesome defect. If calcined for some time before use, flake graphite loses some of its flakiness, and is then more suitable, though never as good for crucibles as the more cubic graphite.

Amorphous graphite does not impart the necessary elasticity to the mixture, so it should not be used, with the possible exception of *colloidal graphite* (known commercially as "Acheson graphite") which has been used very successfully in crucibles for experimental purposes. It appears to be free from the objections to ordinary amorphous graphite.

Ceylonese graphite is much the best; that from India and America is of poorer quality.

In selecting graphite for crucibles attention should not only be paid to the chemical analysis but also to the physical properties, particularly the shape, size, and general structure of the flakes. A poor graphite requires a much larger proportion of clay or other binder.

A specification given by the U.S. Bureau of Mines[1] states the following requirements:—

	Per cent.
Minimum residue after heating 3 min. at 800° C. . .	85
,, ,, on 35-mesh standard screen . .	35
,, ,, ,, 65 ,, ,, ,, . .	50
,, ,, ,, 100 ,, ,, ,, . .	100

Graphite crucibles offer a much greater resistance to metallic oxides and slags than clay crucibles, and last much longer than those made of clay or clay and grog.

For large crucibles, the particles of graphite should be larger than for small ones. If these are not obtainable, it may be necessary to employ sand, or carborundum[2] pot shell to avoid the slipperiness and lamination caused by fine graphite.

The graphite exerts a beneficial action on the clays used in the manufacture of crucibles, making the mixture less sensitive to temperature changes and of greater heat-conducting power.

Another form of carbon in crucibles is obtained (W. Smith's patent, 1920) as described in the section on "Carbonised Bricks." A porous clay crucible may be saturated with a suitable liquid hydrocarbon and fired, with the exclusion of air, so as to produce a similar product. The material produced differs from plumbago crucibles inasmuch as the clay is saturated with minute particles of carbon which are formed *in situ* and can more readily fulfil their purpose (see also "Impregnated Crucibles," p. 587).

Non-plastic oxides such as alumina, magnesia, zirconia, thoria, and beryllia are sufficiently described in Chapter I. and on pp. 590, 595. They should be as pure as practicable, as impurities reduce the refractoriness.

The sizes of the non-plastic particles are important. They should resemble those used for bricks of the same material but omitting all sizes above 0·04 inch.

Preparing the Materials.—It is necessary to remove all roots, stones, and other impurities which can be picked out of the clay, etc., before it is ground. (For methods of *purifying* clays see p. 256.) The "grog" should be similarly examined and any glazed pieces or portions obviously rich in iron or other impurities at once removed. In the majority of British crucible works, this preliminary treatment is carried out in a cursory manner or is omitted altogether: this is a mistake.

The materials must then be reduced to powder of suitable fineness, as described on pp. 261 and 425, each being crushed separately[3] and graded where necessary. They are then stored in bins until required. The clays

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[1] Bull. No. 112, 1920, 38.

[2] Linbarger, U.S. Pat. 1,277,277.

[3] It is not wise to mix the materials and then grind them, as the proportions of each in the final mixture will then depend on the rate at which they are individually ground.

are passed through a fine sieve so as to ensure the binding material being fine enough to spread over the largest amount of surface; this is necessary, as it affects the strength of the crucible. The grog, on the contrary, must be somewhat coarse, as crucibles made of fine grog are dense and strong, but are very sensitive to varying temperatures. The careful grading of any grog which may be used is essential.

Grinding American graphite with a very small proportion of caustic soda and water improves the quality of crucibles in which it is used, but no advantage is gained with Ceylon graphite.

Sillimanite and allied materials, as well as *alumina, magnesia, zirconia,* and *other oxides*, should have been calcined at the highest practicable temperature before use, electrical fusion being advisable. They should be ground to a suitable size or sizes and carefully graded by sieves.

Considerable difference of opinion exists as to the most suitable sizes of particles, and the proportions of each size to give the best results, but Partridge and Lait[1] have found that at least 20 per cent. of particles less than 0·001 mm. should be present, and that it is best if 50 per cent. of the particles are about 0·01 mm. and the rest between 0·001 and 0·005 mm. in diameter.

All the various materials should be carefully dried and weighed out, as required, in the desired proportions. This drying is important, as serious differences in the quality of the crucibles will occur if the materials are weighed in a wet state. A method of measuring out the materials in boxes or barrows is often used, but it is far less accurate than weighing.

Proportions.—The various ingredients used in the manufacture of crucibles are mixed in proportions which depend on the properties the crucibles are desired to possess. For small crucibles which are not to be used under very trying conditions a good fireclay containing about 70 per cent. of silica and 25 per cent. of alumina may be used without any addition. It is, however, desirable to use several clays, and also sand or, preferably, grog.

Grog crucibles are made of 1 part of clay with not more than 2 parts of grog. It is convenient, and sometimes advantageous, to replace one quarter of the grog by old crucibles which have been ground to a coarse powder. If this is done, care should be taken that only the clean parts of the old crucibles are used for this purpose, as adherent slag or other parts of the charge may prove disastrous if mixed in the body of a new crucible.

Sillimanite crucibles (including those of allied minerals, see p. 146) usually have clay as a bond. The low plasticity of the mixture makes slip-casting (p. 611) a suitable process of shaping. A mixture specially suitable for crucibles for melting glasses experimentally consists of:[2]

	Fineness.	g.
Sillimanite (cyanite)	– 100-mesh	400
Ball clay	– 85 ,,	560
China clay	– 100 ,,	320
Calcined alumina	– 100 ,,	480

These substances are mixed and added to a mixture of:

Sodium silicate (sp. gr. 1·275)	12 ml.
1 per cent. sodium carbonate solution	70 ml.
Cellulose extract powder	0·05 per cent.
Water	sufficient to form a slip with a sp. gr. of 1·72 after the mixture has been stirred vigorously for 12 to 14 hours.

J. Soc. Glass Tech., 1936, **20**, 207.

[2] A. E. J. Vickers, *J. Soc. Chem. Ind.*, 1938, **57**, 14.

The *best siliceous crucibles* (including Hessian crucibles) contain equal weights of free silica and clay; this necessitates the employment of a very plastic binding clay.

Plumbago crucibles are usually made of equal parts of clay and graphite, but some are made of 1 part of clay and 3 or even 4 parts of graphite[1] or coke, whilst crucibles for steel and very sensitive alloys contain only 6 per cent. of carbon, usually in the form of coke-dust. The graphite has a much lower relative weight than clay, and so occupies a much larger volume than its weight suggests.

The use of the following mixture (with or without dolomite or magnesite) is claimed in Eng. Pat. 233,986 (1923): graphite 15 to 65, clay 15 to 50, and siliceous material 5 to 15 parts, the crucible being burned at 1094° C. to vitrify the bond.

For *steel manufacture*, crucibles of the shape shown in fig. 122 are used. They generally hold 75 to 80 lbs. of metal and are made chiefly of a mixture of fireclays: the proportions of the ingredients vary with the quality of steel to be made. The following mixtures are used by firms of high standing:—

TABLE XC.—CRUCIBLE MIXTURES FOR VARIOUS METALS.

	For Hard Steel (German).	For Mild Steel (German).	For Razor Steel.	For very Pure Steel.	For Copper Alloys, Brass,[2] etc.		For Cast Iron.	
					a.	*b.*	*a.*	*b.*
Graphite or coke .	54	40	12	3	8	12	53	50
Fireclay . . .	36	38	40	87	67	50	43	40
China clay . . .	..	..	40	10	...	13	..	..
Grog[3] . . .	10	22	8	..	25	25	4	10

The following mixtures are largely used in Sheffield, but it must be clearly understood that each maker works according to his own ideas and alters his recipes whenever there appears any advantage in doing so:—

TABLE XCI.—CRUCIBLE MIXTURES FOR STEEL.

	A.	B.	C.	D.	E.	F.
White china clay . . .	10	20	20	15	..	..
Stourbridge clay . . .	46	40	20	33	47	..
Derby clay	20	18	13	23	..	40
Stannington clay . . .	20	18	40	23	47	28
Coke or plumbago . . .	4	4	7	6	..	4
Grog	..	..	..	..	6	28
	100	100	100	100	100	100

For analyses of these clays see Table LXXXIX.

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[1] A mixture of equal volumes of coke, Stourbridge clay, pipe clay, and grog, together with "a suitable quantity" of plumbago, was patented by T. Callow in 1904. A mixture which is extensively used in Germany consists of 36 measures of fireclay, 23 of coarse grog, 23 of powdered coke, and 18 of graphite.

[2] Some brassfounders prefer crucibles with 50 per cent. of graphite.

[3] The fine particles should be removed from the grog by passing it over a 40-mesh sieve and rejecting what passes through the latter. Crucibles in which no fine grog is used are more durable than others.

When a high carbon steel is to be made, the crucible may contain more graphite than where a mild steel is to be produced. Crucibles with a high content of graphite are objectionable for melting steel, as the metal absorbs flakes of graphite, which become enmeshed in it, producing small holes, flaws, and weak places in the casting. As crucibles containing graphite last longer, they are cheaper to use than those made exclusively of clay. They are employed for all but the highest grades of crucible steel, the proportion of graphite (or coke-dust) diminishing as the quality of the steel increases. Where the proportion of silicon in the steel must be kept at a minimum, very little, if any, china clay should be used in the crucibles, as the china clay, being much finer than the fireclay, is more readily attacked by the steel.

Though nearly every steel melter has his own mixture for crucible manufacture, all agree in preferring several clays rather than a single one, no matter how refractory its character.

The following composition was patented in 1893 by E. J. T. Digby:—A mixture of clay 5 parts, china stone 5 parts, and gas carbon 2 parts is ground and mixed with 17 parts of plumbago which has been passed through a No. 17 sieve and with 2 parts of plumbago which has been passed through a No. 80 sieve. The mixture is kneaded with water so as to form a stiff paste, which is then used for making the crucibles.

The proportions of particles of different sizes should be such as to ensure the crucibles being dense enough to prevent serious penetration by molten metal and slag, and—in plumbago crucibles—to prevent undue oxidation of the graphite. The density should not, however. be greater than is really necessary, or strains will be set up as a result of the sudden changes of temperature which occur when the crucibles are removed from the furnace, and these strains will result in the destruction of the crucible.

For *assaying*, crucibles should be made of (*a*) clays which vitrify appreciably at Cone 9 or below; (*b*) sufficient refractory grog to prevent them from cracking. They must be dense enough to resist the action of highly corrosive slags, but should be sufficiently porous to be capable of fairly rapid heating.

The *scorifiers* made by one of the largest British manufacturers are composed of 6 parts of grog and 5 parts of " plumbago clay," the latter consisting of a mixture of Stourbridge fireclay and local fireclay, with about 10 per cent. of plumbago. Some firms make scorifiers of the same composition as the mixtures used for crucibles, but use fine grog instead of coarse, especially for the smaller sizes.

Alumina crucibles are usually made of alumina with 5 to 10 per cent. of binder (clay, colloidal alumina, etc.—see p. 590). According to Partridge and Lait [1] crucibles which can be used up to 1750° C. can be made by adding pure alumina to a refractory clay so that the final product contains 60 to 70 per cent. of alumina. Such crucibles are highly resistant if their porosity is low.

Magnesia crucibles are made of dead-burned or fused magnesia with 2 to 5 per cent. of hydrated magnesia (preferably colloidal) as bond. For some purposes 5 to 25 per cent. of graphite is added, and for others 15 to 30 per cent. of steatite (see p. 589).

Carbide crucibles are usually made of silicon carbide with 5 to 15 per cent. of binder (clay, felspar, water-glass—see p. 592). Up to 25 per cent. of graphite is sometimes added.

Chromite crucibles are made of the same materials as chromite bricks and in similar proportions, but only selected chromite (not the crude ore) is used.

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[1] *J. Soc. Glass Tech.*, 1936, **20**, 200.

Up to 20 per cent. of magnesia is sometimes added (see "Chrome Spinels," p. 201).

Zirconia crucibles may be made of pure zirconia with 3 to 10 per cent. of binder (p. 593), but as they are porous it is advisable to add about 2 per cent. of magnesia, thoria, yttria, or other suitable oxide (see p. 593). If a slip is to be used for casting it will be necessary to add a little hydrochloric acid (p. 611). Up to 50 per cent. of silicon carbide is sometimes added. E. Rietz has recommended: zirconia 35, graphite 40, and clay 25 parts.

Thoria, titania, and beryllia crucibles are made of fused oxide with 5 per cent. of finely milled (colloidal) oxide as binder (p. 594). Various proportions of other oxides may be added.

Crucibles of mixed oxides are made in many different proportions (see p. 594). One interesting patent (Eng. Pat. 179,928) specifies zirconia 60 to 80 per cent., yttria 13 to 17 per cent., thoria 0 to 10 per cent., and erbia (or beryllia) 5 to 20 per cent.

Mixing.—The various materials, in the correct proportions, must be mixed with water[1] to form a stiff uniform paste. There are several methods of doing this, but the ones most generally used are *treading*, *panning*, and *pugging*, the first-named being chiefly used for large crucibles.

When the materials are to be mixed by *treading*, they are spread out on a concrete floor and are sprinkled with water. The mass is turned over repeatedly with spades and, when it becomes too pasty to be worked in this way, it is again spread out and is trodden by men with bare feet, who squeeze the clay with the heel and centre of the foot or between their toes, and so mix it thoroughly (fig. 127). Each portion of the material has to be squeezed between the toes, compressed, and then pressed on to the previously worked paste.

The treader stands in the middle and, working his toes, goes over the whole surface of the clay in a spiral direction, always working towards the edge. Having reached the edge, he turns round and walks in the opposite direction until he arrives at the starting-point. Some treaders prefer to walk in straight lines instead of in a spiral direction.

The trodden mass is then made up into balls of 40 to 45 lbs. weight, and is afterwards beaten into a dense mass. In some works it is pugged after being "trodden."

The mixing is made more effectual if the material is "trodden" once, then cut up and turned over with a spade, afterwards re-trodden and again mixed with spades. The mixture is then made into rough blocks or balls (fig. 128), each of which is sufficient to make one crucible.

To prevent the mixture hurting the feet of the workmen, some crucible makers only have the clays trodden as described above, any sand, etc., being added afterwards and mixed with the aid of spades. This procedure is undesirable so far as the production of a good mixture is concerned, and, if the material is too rough for all of it to be trodden together, it should be treated in a pan-mill.

For additional precautions in treading clay see under *Mixing* (Chap. XIII.).

In the Buckley district, the fireclays were formerly "trodden" by horses, but, at the present time, a mechanical "treader" is used. This consists of a large pan 16 to 30 feet diameter and about 2 feet deep, with a revolving beam fitted with a series of "legs" which are set in motion by means of an overhead arm.

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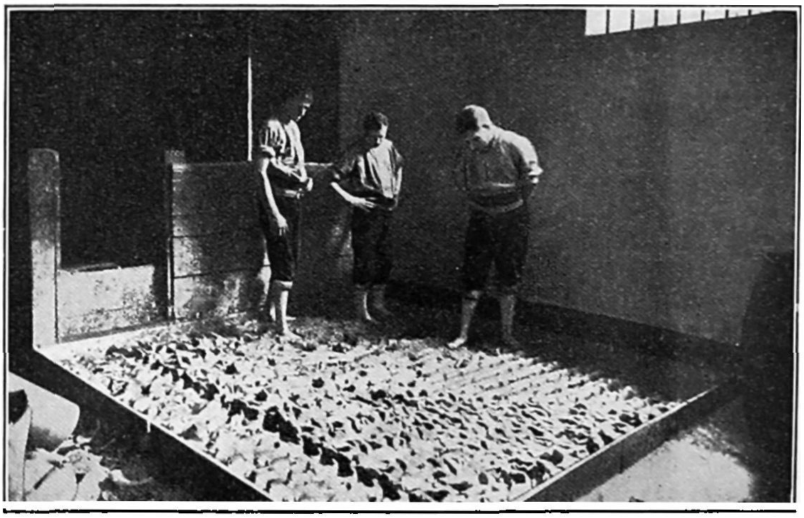
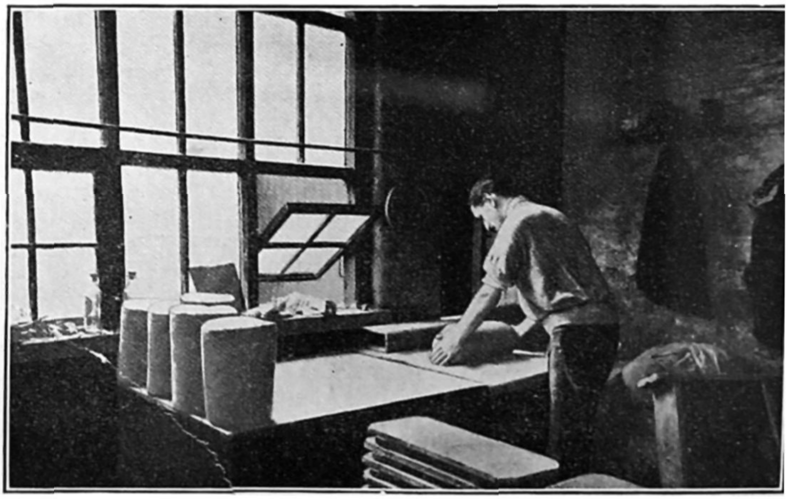
[1] Some manufacturers prefer to use mineral oil instead of water, in the belief that it produces a more plastic paste.

After treading, the clay is " balled " by throwing it repeatedly and with violence on a bench so as to consolidate it and drive out as much air as possible.



(By the courtesy of Messrs. E. Allen & Co., Ltd.)

FIG. 127.—Treading clay.



(By the courtesy of Messrs. E. Allen & Co., Ltd.)

FIG. 128.—Moulding clay for crucibles.

Various firms have endeavoured to replace treading by means of pug mills or open mixers, but without much success, the makers declaring that clay mixed mechanically does not suit their purpose so well as that which has been trodden. The reason for this is difficult to understand, as a mechanical mixer effects a much better distribution of the particles and produces a sounder mass. In two cases known to the author, the use of mixing machines has proved quite satisfactory, but they were only introduced after strong opposition. One difficulty is the stiffness of the clay paste; when mixed mechanically it is usually too soft, but by using a specially designed mixer this objection may readily be overcome.

French crucible manufacturers mix the dry materials together and then pass them through a pug mill, water being added to the contents of the latter by means of a sprinkler. The paste is allowed to " sour " for several days and is again passed through a pug mill, this process of " souring " and pugging being repeated several times. Some German manufacturers adopt this method for all crucibles. It is also used extensively in the U.S.A., though, in the latter country, crucibles made from a semi-dry material are popular.

The plasticity and working properties of a crucible mixture are greatly affected by the presence of very small quantities of certain substances, such as acids and alkalies. It is well known that such substances (electrolytes) increase or diminish plasticity in all clays, but the subject has been investigated with special reference to graphite crucibles by H. G. Schurecht, who found that electrolytes are sometimes added to the materials used for making crucibles. The addition of sodium hydroxide caused a body, composed chiefly of flake graphite and Dorset ball clay, to lose its plasticity, but a similar body containing American (Mississippi) bond clay was improved. The addition of very little hydrochloric acid improved the working properties of the Dorset clay mixture. The addition of sodium hydroxide to bodies containing Dorset clay at first decreased their transverse strength, but with larger proportions the strength was increased, probably on account of the deflocculation of the clay enabling a dense body to be formed. With the American clay, sodium hydroxide increased the strength. When the graphite was ground with sodium hydroxide prior to mixing it with the clay, a notable increase was obtained in the strength of the body. Small additions of sodium hydroxide decreased the density of bodies containing Dorset clay but increased it in those containing Mississippi clay. With larger additions, the opposite effect was produced. The shrinkage of bodies containing Dorset clay was first decreased and then increased by the alkali, but in those containing American clay the shrinkage was increased throughout.

The author has made many careful physical and other tests of the same materials treated (*a*) by treading and (*b*) in a wet pan mill, and has always found that the mechanically mixed material is more uniform and homogeneous in texture than that which has been trodden. Yet so conservative are the users of steel crucibles, and so serious is the loss occasioned by defective ones, that only a very small number of firms use a mechanical mixer, notwithstanding the fact that it can be made to produce a better material at a lower cost.

For small and medium-sized crucibles, the materials are mixed in a trough mixer or pug mill, or, preferably, by *panning.* For the latter purpose, sufficient quantities of each material to form a " charge " for a pan mill are weighed out, placed in the mill, and the latter is set in motion. The necessary quantity of water is then added slowly through a sprinkler attached to the mill, and the pan is kept in motion until the materials are properly mixed. In most cases, half an hour's treatment is sufficient, but for special crucibles the mixture is sometimes panned for several hours.

The paste is allowed to remain in cellars for several days in order that it may " sour " and its plasticity be fully developed. At the same time, it may, if too soft, be allowed to dry partially, so as to produce a paste of the desired stiffness. The paste may then be placed in a small pug mill, the material passing out of the latter being cut into clots each large enough for one crucible. Some makers pass the paste twice or three times through a pug mill, but so thorough a treatment is not usually necessary.

The "souring" is an important part of the preparation of the mixture, during which the clay becomes more plastic, the moisture is distributed uniformly, and various chemical reactions occur. The effects of souring are increased if the material is pugged repeatedly during the souring stage.

During the souring, the surface of the paste is prevented from drying by covering it with cloths which are kept constantly wet.

In each of the foregoing methods great care is needed to add the correct proportion of water; too much water must be avoided, or the mass will shrink unduly in drying, whilst, if too little water is present, the material will not be sufficiently strong, owing to the binding power of the clay being imperfectly developed. Some firms use warm water in preference to cold and claim that it produces a more plastic mixture.

The materials used for plumbago crucibles are usually mixed in an edge-runner mill, perferably one in which the run travels transversely across the pan as well as rotating in the usual manner. Several hours' milling is necessary to produce a really good mixture, and much longer if the materials are not fed properly to the mill.

It is usually best to mix the graphite and clay first and to add the sand through a coarse sieve much later.

The mixed materials should be allowed to "sour" in a cool place for about a fortnight, after which they may be pugged twice—preferably in a pug mill lined with bronze and fitted with bronze knives—and the paste so produced may be extruded through a mouthpiece attached to the pug mill.

The extruded mass is broken into large clots, each sufficient for a crucible; these are "bumped" on a bench to give them greater density and are then ready for moulding.

Several patents mentioned in Chapter V. are also applicable to the manufacture of crucibles.

De-airing.—The de-airing process—which consists in passing the clay-paste through a double pug mill with an intermediate shredding device and a vacuum chamber—greatly increases the plasticity and workability of the paste, as well as prevents the formation of air-blisters in the crucibles. De-airing greatly increases the quality of crucibles, imparting greater toughness, greater resistance to abrasion and corrosion, a better finish and, in many instances, a greater resistance to spalling.

Consistency.—Most crucibles are made of a plastic paste, which should be as stiff as possible consistent with good working. For some purposes a granular powder containing about 7 per cent. of water is preferred, the crucibles being then shaped in a press under a much higher pressure than is needed for a paste.

Some crucibles are preferably made of *slip*, *i.e.* a suspension of the various materials in water so as to form a fairly "thick" or viscous fluid. The preparation of such slips is described on p. 612.

Making.—Crucibles may be made (1) by hand in moulds, (2) by "throwing" on a wheel, (3) in jiggers and jolleys,[1] (4) in presses, or (5) by casting.

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[1] This method is specially used for plumbago crucibles, but if granular plumbago is one of the ingredients, the material should be in an almost dry state and should be shaped in a wooden mould. Flaky graphite is not subject to this limitation.

Hand-moulding is usually confined to the larger crucibles, as it is a slow and somewhat costly process, but gives excellent results. In making crucibles for melting steel, the wooden or cast-iron moulds are technically known as " flasks " (fig. 129). They consist of an outer " flask," the inside of which is the shape of the exterior of the crucible, but has an opening rather more than an inch in diameter at the bottom. The interior portion or " stopper " forms the core of the mould and is provided with a handle, so that it may be worked about until the paste in the flask is properly compressed into shape. The stopper has a projecting piece at the bottom. This passes through the hole in the bottom of the flask, and serves as a pivot and to keep the core in position during the shaping of the crucible.[1]

The flask is well oiled, the paste put into it, and then gradually forced to the desired shape by inserting the oiled core and working it to and fro in a rotary manner. If desired, the clay may be added in several portions instead of all at once, each addition being worked into place before the next is added.

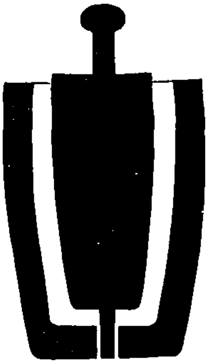
Fig. 129.—Flask.

When the paste has been properly compressed, any superfluity is cut off, the core or " stopper " is withdrawn, and a blunt knife is inserted between the clay and the outer " flask " so as to form the contracted mouth of the crucible (fig. 122), which enables it to be more readily covered in the furnace, protecting the surface of the metal to some extent from oxidation, and serving several other useful purposes. Some makers prefer to effect this shaping of the mouth of the crucible after it has been taken out of the mould by rotating it on a small table, somewhat resembling a potter's wheel. Others turn the mouth of the crucible inwards by pressing an inverted " turning dish " over it.

The greatest care must be taken in filling up the hole at the bottom of the crucible and in making good any defects in other portions. It is always difficult to secure an absolutely satisfactory joint or patch, and any carelessness in this respect may lead to the loss of a considerable quantity of molten metal.

In another method of hand-moulding, the mould consists of a block of dense, close-textured wood, which is covered with a wet cloth free from loose threads. The mixture is thrown on this with some force and in small handfuls at a time, until a solid and uniform mass of suitable thickness is obtained. The mass must be repeatedly kneaded and stabbed so as to secure the absence of weak places, air-bubbles, etc. The thickness of the bottom of the crucible should be about twice that of the sides. The bottom of the crucible being prepared, it is lifted on to a sanded board, placed quite level, and covered with a linen disc. The drum or sides of the mould[2] are fastened to the board and the paste worked around the sides. If the crucible is sufficiently large, this may be done with the feet; otherwise, the hands or a small rounded stick is employed. The surface is then roughened with an iron comb and fresh clay thrown on to the mould, handful by handful, until, after sufficient kneading and working, the mould is lined with paste to the requisite thickness. The inner surface of the crucible is then smoothed with hand tools.

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[1] Unless the plunger is guided by the projecting piece, it is difficult to make large crucibles of regular shape.

[2] A similar mould, used for glass pots, is illustrated in fig. 152.

In a third method of moulding crucibles by hand,[1] the clay paste is thrown on to a hollow wooden core, the shape of the interior of the crucible (fig. 130), and mounted on a vertical steel spindle so that the core may be rotated by hand or power. The workman forms the outside of the crucible by working the paste with his hands or with a tool, at the same time as the core rotates. A sliding vertical gauge or a profile may also be used to ensure the crucibles being accurate in shape and thickness. When the shaping is finished and the crucible smoothed, the core is lifted from the spindle and inverted over a board. The crucible then easily slips off the core, and the latter is again ready for use. A linen cover may be put over the core to facilitate the removal of the crucible. The pouring spout is made by pressing part of the edge of the crucible between the thumb and fingers.

Plaster cores are occasionally used in this method instead of wooden ones, but they are costly and not particularly advantageous. The chief reason for their use is that the crucible separates more readily from plaster than from wood, but with a skilled workman plaster confers no advantage.

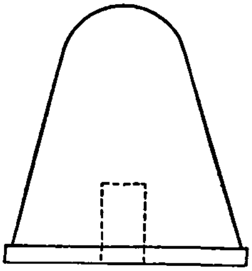

FIG. 130.—Crucible core.

For shaping crucibles made of non-plastic materials, the moulds may consist of a steel cylinder with a flanged steel core. Just sufficient water is mixed with the powder to enable the mixture to flow when tamped. Larger moulds may be in three pieces. A piece of brown paper should be inserted as a liner. It prevents the crucible from being torn when the mould is removed.

Crucibles made of pure alumina powder, damped, moulded by tamping and fired at 1500° C. are fragile, but satisfactory. They must be fired on a bed of loose alumina powder to allow for creeping.

Throwing is particularly useful when only a few crucibles of a special shape are required. A lump of paste is placed on the potter's wheel, and is worked to the desired shape by the hands of the potter, whilst the wheel is rotated at a moderate speed. The paste which gives the best results, so far as the durability of the crucibles is concerned, is too stiff to be " thrown " readily, so that this process is of very limited application in the manufacture of crucibles.

Throwing is an excellent method of manufacture for small crucibles when the men can be relied upon, but, as the variations in thickness and shape depend entirely on the thrower's skill and judgment, manufacturers not unnaturally prefer a more mechanical process.

Crucibles are made in large numbers by means of a jolley and jigger (fig. 131). A piece of paste is placed in a plaster of Paris or iron mould, which is then rapidly rotated, and a profile or jigger is pressed on to the clay so as to make it conform to the interior of the mould and produce a crucible the walls of which are of the requisite thickness. The mould is then removed from the machine and taken to the dryer, its place being taken by a fresh one. This is a good method, but somewhat costly, owing to the frequent renewals of the plaster moulds. It has also the drawback that the clay paste must be very soft, and the crucibles are not as dense as desirable.

Mechanical presses for crucibles are of two kinds: those driven by hand and those which are power-driven.

Hand presses are more suitable for small crucibles and scorifiers, but are occasionally used for large ones. That shown in fig. 132 is of the screw type,

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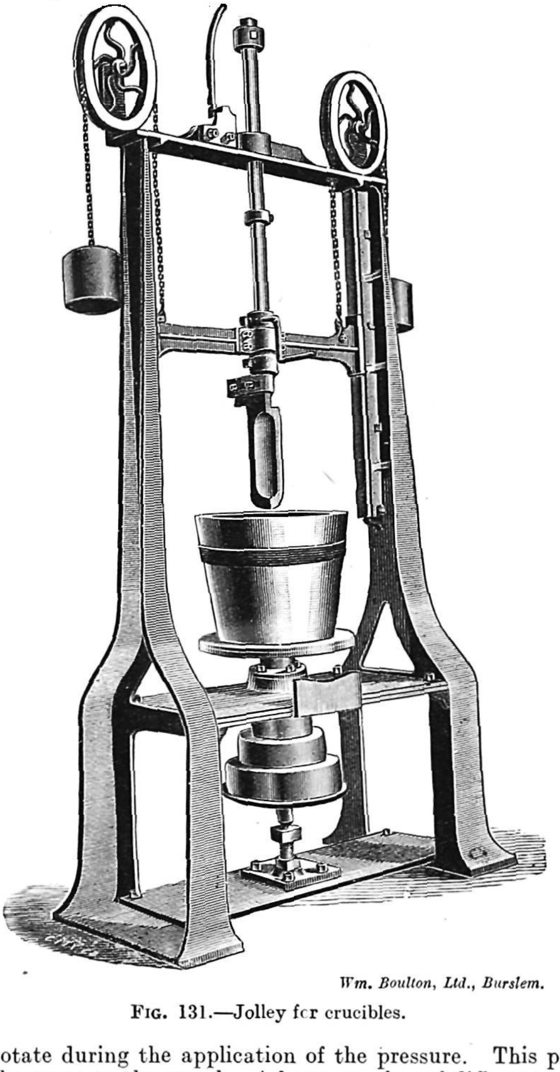
[1] This is a combination of hand-moulding and throwing.

and is similar to that shown in fig. 116. They consist of a plunger and lower mould or die, the paste being placed in the die and then compressed by the plunger.

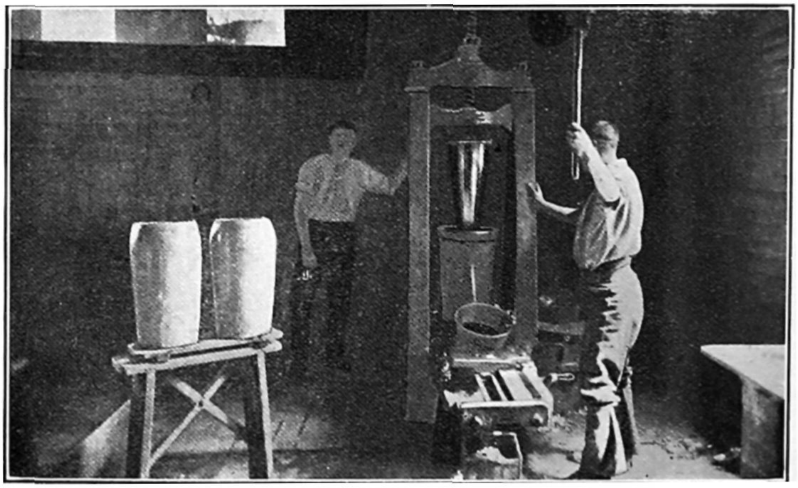
In power-driven presses (fig. 133) either the plunger or die, or both, may be made to rotate during the application of the pressure. This prevents the adhesion of the paste to the metal. A large number of different presses have been suggested for the manufacture of crucibles, but most of them are unsatisfactory because they make the various parts of the crucible irregular, some being much denser than others, thereby setting up strains and cracks. The author has made an extensive series of trials with all the advertised presses (both British and foreign ones), and has concluded that the most



Wm. Boulton, Ltd., Burslem.

FIG. 131.—Jolley for crucibles.

suitable press consists of a rotating plunger and a loose mould which is lifted by a treadle to the plunger. The sides of the plunger are slightly flattened and grooved so as to permit the escape of air between the plunger and the clay. The mould or die is carried on a plate which can be rotated on an oiled bed or on ball bearings. This plate is not driven mechanically, but is caused to rotate by the friction between it and the clay. To use such a machine,[1] a piece of stiffish clay paste of suitable size is dipped in paraffin and placed in the mould. The treadle of the machine is then depressed and the mould is lifted until the clay is forced against the rapidly revolving plunger. As the mould rises, the clay is gradually squeezed into the desired shape and the friction causes the mould to rotate rapidly. When the rising mould has reached its highest point, the surplus clay is cut off automatically by the pressure of the top of the mould on the lower side of the plunger head.



(By the courtesy of Messrs. E. Allen & Co., Ltd.)

FIG. 132.—Hand-driven crucible press.[2]

The treadle is released and the mould then descends; when a suitable point is reached, a stop comes into operation and prevents the crucible from descending further, while permitting the mould to do so. The crucible is then removed and the machine is ready to make another. A daily output of 6000 crucibles, each 6 inches or less in diameter, or 1400 crucibles of 12 inches diameter, can easily be obtained with one of these machines and two strong youths. The clay is supplied in the form of discs, which are made in a small pug mill fitted with a circular mouthpiece and a wire-cutting table. This arrangement saves the necessity of weighing out the clay.

All machines with plungers and dies which do not rotate appear to be unsatisfactory for any but the smaller sizes of crucibles, as their output is

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[1] Fig. 132 is a press similar in many respects to the one described in the text, but differs from it in several details. The one described is not "on the market," though used by several firms.

[2] The press shown is an improvement on the Crowley's screw press which has been used in Sheffield for over fifty years.

lower, the quality of the crucibles is inferior, and much trouble is caused by the adhesion of the clay to the metal.[1]

Nevertheless, John Whitehead & Co., Ltd., Preston, introduced a power-driven crucible press in 1932, which has been used successfully though neither the plunger nor mould revolves.

Crucibles made of zirconia and similar oxides are sometimes made by tamping or pressing the material in a *graphite mould,* in which they remain whilst being baked prior to the final burning. It is claimed that such crucibles are as hard and strong as those made by slip-casting.

In all mechanical presses used for crucibles it is necessary to dip the lump of paste into paraffin or other lubricant, unless the mixture is so rich in graphite that no other lubricant is needed. Unless the clay is well lubricated, it will adhere to the metal of the machine, and will cause difficulty in making crucibles of good shape.

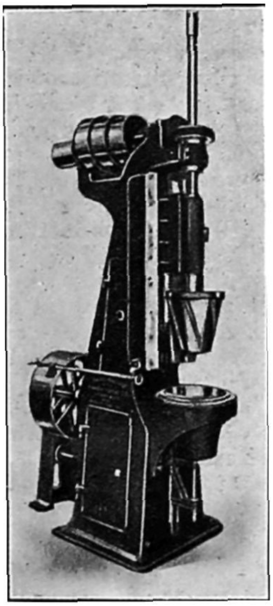
When a dry or semi-dry powder is used, the pressure required may be as much as 200 tons per square inch (occasionally even more). With such high pressures a bond is seldom needed.

The most appropriate pressure depends on the nature of the material as well as on the sizes of the particles and the consistency of the mixture. Thus, the pressure applied to the stiff-plastic paste used for zirconia crucibles should be about 40 tons per square inch.

Casting is a term applied to two processes used in the manufacture of crucibles:

(i) *Slip-casting,* in which a slip or slurry of suitable consistency is poured into a plaster mould until the latter is full. After a suitable time, the surplus fluid is poured away, and the mould will then be found to contain an article of the required shape. It must be carefully dried and then burned before it is fit to use.

(ii) *Electro-casting* or *fusion-casting,* in which the material is fused and is afterwards poured into moulds made of sand and allowed to cool slowly. This latter is the more suitable for crucibles of the very best quality, but such crucibles are very expensive, so that moulded, pressed or slip-cast crucibles are much more common.



Baird Machine Co., Detroit, Michigan.

FIG. 133.—Power-driven crucible press.

Slip-casting is a process offering great possibilities for the manufacture of crucibles from mixtures very rich in non-plastic materials.[2] It consists essentially in making the materials into a fluid or slip and pouring this into a plaster mould, but various modifications are possible.

In one method of casting crucibles, the mould is filled with the slip and

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[1] To overcome this, H. L. Doulton, in 1883, patented the use of a cloth bag of the same shape as the interior of the mould, and fitted with a metal rim to facilitate its insertion into, and removal from, the mould. In 1880, W. R. Lake patented the use of removable moulds, the crucible being dried in the mould in which it is made so as to prevent the distortion which often occurs. The arrangement is good in this respect, but it is slow, as each fresh mould has to be placed accurately in register with the plunger before a crucible can be made. It is also costly on account of the large number of moulds employed.

[2] Highly plastic mixtures cannot be cast satisfactorily, and, if a highly plastic clay is considered to be an essential ingredient, it should be lightly calcined before use.

allowed to stand for a short time. The superfluous slip is then poured out, leaving a mass of paste of the desired shape in the mould. The mould with its contents is then taken to the dryer and, after a short time, the crucible will be sufficiently firm to be removed from the mould.

A less satisfactory method of casting consists in placing a mould on a rapidly rotating table or jigger, and then pouring an ordinary slip into it. The centrifugal force causes the slip to collect around the sides of the mould in a uniform manner, and the greater part of the water is forced into the pores of the plaster. This is much quicker than the ordinary process of casting in stationary moulds, and enables crucibles with thicker walls to be produced.

The mere addition of water to an ordinary clay mixture is not sufficient to produce a good slip. On the contrary, to obtain the necessary fluidity far more water than will make good crucibles would have to be used. The smaller proportion of water required to make the slip satisfactory may be made sufficient by adding a small proportion of certain salts in solution, so as to make the clay fluid. This fact was discovered in Staffordshire in 1740 to 1750, but its value for the manufacture of crucibles is an outcome of Weber's investigations in 1906 and succeeding years. The effect of various salts on the fluidity of clay slips is also described on p. 106.

Weber (English Patent 6560—1909) uses lime-water, baryta, or a mixture of lime-water and caustic soda, and adds it to the water to be used for mixing with the clay, etc. The latter is then fed into this dilute alkaline solution at a regular rate, the mixture being stirred mechanically so as to secure a thorough mixing of the two. The mixture is then run into a second vessel or reservoir, and, after remaining stationary for a short time, the slip is run off into moulds.

Weber recommends the following proportions (all by weight):—

(*a*) 450,000 parts of a dry mixture of Stourbridge clay and grog, 350 parts of barium hydrate or 220 of barium carbonate, 120,000 parts of water and 600 parts of caustic soda, or the equivalent amount of carbonate or silicate.[1]

(*b*) 380,000 parts of grog, 630 parts of barium hydrate, 100,000 parts of water, and 800 parts of silicate of soda.

The barium hydrate is added in sufficient quantity to precipitate the sulphates and soluble carbonates, which would otherwise interfere with the action of the alkalies.[2]

When properly prepared, a casting slip made by Weber's process remains fluid so long as it is stirred, but soon sets to a gelatinous mass if it is left undisturbed. This gelatinisation may be avoided by adding an organic colloid such as tannic acid, humic acid or lignite at the same time as barium carbonate.[3] The most suitable electrolytes are caustic soda, sodium carbonate (in various forms), sodium silicate, and sodium aluminate in the proportion of 0·03 to 0·50 per cent. of the weight of the clay. For each clay there is an optimum proportion of electrolyte.[4]

In England, it has become customary to use a mixture of sodium carbonate and sodium silicate, a mixture of equal proportions of these two substances being employed. Casting slips have the greatest viscosity if the sodium

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[1] A mixture of water-glass and soda is sometimes preferable to soda alone.

[2] Very small proportions of sulphates in a clay may increase its viscosity and cause partial flocculation, with resultant irregularity in the composition of the ware. As small a proportion as 0·002 per cent. of calcium sulphate will sometimes spoil a clay. Fortunately, the addition of barium carbonate effectively precipitates the sulphates and renders them and also any soluble calcium ions harmless. Precipitated barium carbonate is preferable to barium hydroxide.

[3] Singer, *Brit. Clayworker*, 1938, **47**, 151.

[4] See footnote (1), p. 613.

carbonate is added first and is followed by the sodium silicate. A minimum viscosity is obtained if the sodium silicate is added first, and an intermediate viscosity if the silicate and carbonate are added simultaneously.

Each clay mixture may, as shown by Weber, require special consideration with respect to the proportion of salts added, and Wright and Fuller have found that, whilst 2 parts of sodium carbonate to 1 part of sodium silicate is useless for the materials they required to cast, 1 part of sodium carbonate and 2 parts of sodium silicate gave a heavy slip which, whilst casting in 11 to 14 hours, showed much flow and lamination in the interior. These investigators found that 4 parts of sodium silicate to 3 parts of sodium carbonate gave the best results. Riddle, on the contrary, found equal parts of the two salts quite satisfactory. With some clays, sodium carbonate and sodium silicate are not satisfactory, but sodium tannate, sodium gallate, and sodium gallotannate produce excellent slips, in some cases with, and in others without, soda.

When clay is present, the electrolyte used must be an alkali or solution; with most non-plastic oxides, on the contrary, an acid—preferably hydrochloric—must be used. Clays or mixtures which contain little protective colloid do not cast readily. This difficulty is avoided by adding a protective colloid such as gallic and tannic acids and their sodium salts, and also a little (0·1 per cent.) tannic acid instead of the usual electrolytes.

Böttcher has shown that the electrolytes used act only within very narrow limits of concentration, so that equal care must be taken to avoid either an insufficiency or an excess, with the exception of ammonia, which can be used within much wider limits. Usually 5 or 6 times as much carbonate as hydroxide is required. Potash is much weaker than soda in its suspending action. The chief precautions required are: (i) to avoid an excess of soda [1] or other liquefying agent; (ii) to have the slip at a suitable temperature, and (iii) to secure uniformity by means of a thorough stirring or shaking (usually in a blunger). The order in which the various ingredients are added sometimes affects the product, and the best order must be found by trial. It is usually best to begin with the water and soda or other electrolyte, then to add the clay or other binder and only after ample agitation to add the non-plastic materials.

It is also important to ascertain what are the best viscosity and specific gravity of the slips, as these properties vary with different materials. A sp. gr. of 1·83 is suitable for many slips, and approaches the maximum for many bodies when water-glass or sodium carbonate is used. With gallates and tannates a higher specific gravity is practicable but seldom needed.

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[1] An excess is to be avoided because it may thicken the slip unduly, and so spoil it by a process of flocculation. According to Simonis, the simplest method of ascertaining how much water and soda (or other compound) is required for a given clay is to make a ½ per cent. solution of soda or baryta or of the mixed salts it is desired to use and to make a series of tests as follows:—

Exactly 2 ounces of the clay to be tested is weighed and placed in a tall 8-ounce bottle together with 1 ounce of water and a suitable, measured volume of the solution is added. The bottle is then corked and its contents shaken vigorously until a slip is formed. This is allowed to stand for a short time, when, if any precipitation or deposit occurs, it is a sign that either too much or too little solution has been added. A fresh test must then be made with more or less of the solution, and the process repeated until a mixture is obtained which is sufficiently fluid and which retains the whole of the clay in suspension. This mixture will probably be the one which will give the best results in casting.

Sometimes the use of half as much water as clay may prove excessive; if so, a smaller proportion of water must be employed. On the other hand, a larger quantity than that specified may give better results. The best proportions of water can only be ascertained by actual trial.

If the apparatus is available, a still better method of controlling the slips is to determine the hydrogen-ion constant or *p*H-value.

Care should be taken to use a slip of ample fluidity with a minimum of water: in clay-wares it is usually possible to make slips containing less than 25 per cent. of water. An excess of water tends to permit the suspended matter to settle unduly and to shrink excessively during the drying of the article.

To cast crucibles of 2 inches or more in thickness a double mould (*i.e.* a mould and a plaster core) must be used, so that water is withdrawn from both surfaces simultaneously.

In order to make up for the water absorbed by the plaster it is necessary, with thick articles, to provide more slip than the mould will hold at first; the surplus is usually contained in a funnel and tube attached to the mould in such a way as to prevent an overflow.

The process of casting large crucibles, glass pots, etc., may be greatly facilitated by surrounding the plaster mould with a hollow metal casing and pumping out the air between the plaster mould and the casing. By this means the slip or body adheres much more readily to the mould and a better article is produced in less time. This use of a so-called *vacuum mould* was devised by B. J. Allen (Eng. Pat. 110,649).

The rate of casting may also be increased by making use of the phenomenon of cataphoresis, whereby clay, etc., suspended in water is made to travel in any desired direction under the influence of an electric current. According to B. J. Allen, such a process is particularly advantageous for making crucibles from slips heavily charged with non-plastic material, such as silica and graphite, which cannot be cast in the ordinary way. In this case, the material to be deposited is made into a suitable slip with the addition of a sufficient quantity of acid or alkali and water, and is poured into a mould. It is often easier, but not essential, to use an absorbent mould, as the material may be deposited directly on the metal electrode, which is shaped to give the desired form to the article. An electric current is passed through the mould and slip by connecting one wire to the outside of the mould and another to a brass electrode immersed in the slip. The direction of the current must be such as to cause the particles in suspension to travel towards the outside of the mould, and they are eventually deposited on its interior. A clear liquid accumulates around the immersed electrode, and may be siphoned off, leaving the clay or other material deposited in the required shape. On reversing the electric current, the density of the deposit may be reduced, or the attracting electrode may be applied to parts of the deposit which are required to be the thickest and the repelling (internal) electrode to those which are required to be thinnest. Reversing the electric current also facilitates the removal of the article from the mould. The current required is about 50 to 70 amperes at 50 to 100 volts, depending on the material to be deposited.

Non-plastic materials such as magnesia, alumina, zirconia, thoria, etc., are best shaped by slip-casting. The same method (with minor variations) is used for all these oxides. Thus, for the manufacture of *fused alumina crucibles*, D. Turner[1] has recommended that powdered alumina be ground in a steel end-runner mill for 4 to 5 hours, each charge consisting of 600 g. of alumina and 480 c.c. of water. An excess of hydrochloric acid is then added and the slip heated to 90° C. until all gas is removed. After 48 hours' settling, the greater part of the liquid is poured off and the residue is washed twice with dilute acid, the solid matter being allowed to settle after each washing.

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[1] *Trans. Cer. Soc.*, 1934, **33**, 40.

Hydrochloric acid and water are then added until a slip of N/1 acidity (36·5 g. of HCl per litre) and of suitable casting consistency is obtained.

Partridge and Lait[1] use a Plauson (colloid) mill, a charge of 2 kilos. of alumina and 5 litres of water and, after allowing the slip to settle, decant the surplus water and add hydrochloric acid to make a 10 per cent. solution. This slip contains 40 to 50 per cent. of alumina.

The hydrogen-ion concentration ("acidity") of the slip must be adjusted to a *p*H between 2 and 5 (see Eng. Pats. 382,071, 391,703, 396,234, 405,978, and 410,988).

Where it can be used, an acid-free slip has the advantage of not corroding the moulds and is therefore much cheaper to use. It is made in the same way as the acid slip, but the final addition of acid is omitted. An acid-free slip adheres so tenaciously to plaster moulds that it cannot be removed unless the freshly made article be caused to shrink rapidly by quickly heating it internally with a Bunsen flame. The casting from an acid-free slip is more difficult and uncertain than when an acid slip is used, but crucibles can be cast with thicker walls.

For less refractory crucibles, the oxide is first ground to a very fine powder and is then thoroughly mixed with a suitable proportion of colloidal zirconia or other binding material, and with sufficient water to form a fluid slip weighing about 30 ounces per pint. For comparatively thick-walled articles the slip is then poured into a plaster mould, the water being gradually absorbed into the plaster and leaving a layer of solid material on the interior of the mould. When this layer is sufficiently thick, the superfluous slip is poured off and the mould allowed to stand in a warm place until the article has shrunk away from the sides of the mould and can readily be removed.

When very thin-walled articles are required, an inside mould or core of wood is coated with paraffin wax, and the slip is painted on the wax in as thin a layer as is desired. When the layer has become sufficiently dry, the paraffin wax may be melted and the articles removed from the core. Podszus states that, by this method, he has obtained crucibles with walls only 0 004 inch thick.

Another method consists in making a mixture of the oxide with china clay and water, with or without an electrolyte, pouring this slip into plaster moulds and pouring out the surplus slip after a suitable time. Crucibles made in this manner are less refractory as the clay tends to act as a flux.

When slip-casting oxides, it is sometimes an advantage to use moulds previously warmed to 30° C. and to reject the first two or three crucibles made in a new mould.

To make crucibles employed in investigating emission spectra and other experimental work at very high temperatures, Fritsche, Wahlin, and Oesterle[2] use fused thoria, ground to a fine powder and mixed with a solution of thorium nitrate or chloride to form a paste; this is moulded in a brass mould with a core of Wood's metal to shape the interior of the crucible. After drying and heating, the molten metal is poured out and the crucible is heated in a high-frequency induction furnace to 1600° C. and then cooled to a red heat. Such crucibles are weak through lack of vitrification and require very great care in handling. To strengthen them by adding a different bond would, however, reduce their refractoriness.

Casting molten material has been used successfully for crucibles made of mullite, sillimanite, and allied materials, as well as for those made of magnesia,

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[1] *J. Soc. Glass Tech.*, 1936, **20**, 205.

[2] *Electrochem. Soc.*, Preprint 64, 1933, 11.

zirconia, and other oxides. The material is usually fused in an electric (arc) furnace and poured into moulds made of sand with iron sheets. The filling of the moulds is difficult with small crucibles but much easier with larger ones. Great care is needed to ensure thorough annealing, or the crucibles will be unreliable.

Further information on casting will be found on pp. 651 to 654.

Removing from Moulds.—Clay crucibles can be removed from wooden moulds shortly after production. Crucibles made in plaster moulds should remain sufficiently long for the crucible to shrink slightly and so facilitate removal. Sometimes the moulds are warmed to 30° C. in order to dry them partially and so hasten the shrinkage which is necessary for easy removal.

Crucibles made by slip-casting should be partially dried in the moulds—sometimes a couple of hours suffice—before they are removed.

Some fragile crucibles are made in graphite moulds, in which they are dried and afterwards baked.

Finishing.—The best crucibles are usually "finished" or "fettled" by rubbing the surface with a wet sponge and with leather or rubber so as to make it smooth. Sometimes they are "washed" with a slip of fine clay so as to produce a fine coating inside. This treatment makes the crucibles more resistant to slags, etc., as it is similar to a special lining.

Crucibles used for experimental purposes are sometimes made roughly to shape, baked and afterwards finished by turning on a lathe or by grinding.

The men engaged in finishing should examine each crucible carefully; any misshapen ones and those which vary greatly in the thickness of the walls should be discarded, as they are almost certain to crack when in use.

Drying.—Crucibles must be dried slowly and uniformly, or they will crack when in use. It is specially necessary to protect them from all draughts and from direct sunlight, as these would cause fine cracks. They are usually dried on racks in rooms heated by steam pipes or by heat radiated from the kilns or ovens in which the crucibles are to be burned later. In some works, the crucibles are first placed in a room kept at 30° C. (86° F.), and are then transferred to another kept at 50° C. (120° F.), where they remain for a fortnight or more.

Another method of drying consists in placing the crucibles on racks in small unventilated chambers or stoves, which are then heated by steam until the crucibles are almost dry. The drying is completed by stacking them on racks around the kiln or oven.

Crucibles for melting steel are usually placed on shelves around the walls of the shop in which they are made, each shelf being wide enough to hold two or three rows. They are turned occasionally, and, when nearly dry, may be taken to the furnace room, where they are stored on shelves (fig. 134) until perfectly dried by the heat radiated from the furnaces and castings.

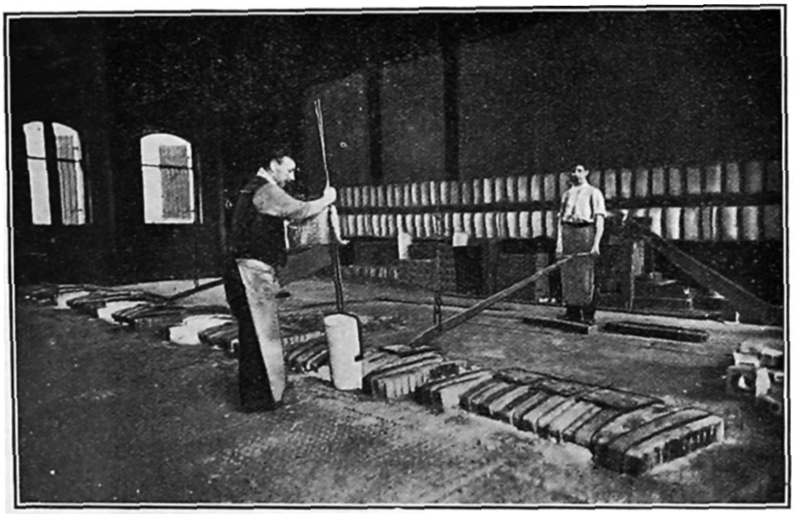
Direct heat should be avoided in drying, and crucibles for steel should not be placed too near the fire until they are perfectly dry. This takes about three months in all, the first month being spent in the making room and the last two in a store, where a small amount of heat may be admitted. The longer the crucibles remain untouched, the better they are likely to prove in use, so that prolonged storage is more profitable than it appears to be at first sight.

Plumbago crucibles are dried for twenty-four hours and then "sleeked" or "sponged over" to give a smooth, dense skin. The drying is then completed. When properly dried, they should emit a clear metallic tone on being struck.

Crucibles made of zirconia and similar oxides are usually dried first at room temperature and later at 120° to 150° C.

Dry crucibles must be kept in a warm place, as they are very sensitive to frost. On no account should they be stored in an open shed.

Burning.—Where crucibles are manufactured in the works in which they will afterwards be used, they are not burned in kilns, but are "warmed through"[1] in the furnaces in which they are to be used, or in a preliminary furnace consisting of a long, low chamber (fig. 135), with a fireplace at one end in which coke is burned. The crucibles are placed on fireclay stands; they are slowly raised to a red heat and are then allowed to cool slowly. Other types of furnace are also used for other kinds of crucibles.



(By the courtesy of Messrs. E. Allen & Co., Ltd.)

FIG. 134.—Crucibles drying on shelves.

This first heating is very important, as it is at this stage that the strains which may cause the crucible to be defective are usually produced. The present custom of allowing the user to fire his own pots is, on the whole, satisfactory, as it limits the range of dispute in case of damage. There is no firing in the strict sense of the term, the pot being gradually warmed, then placed in the furnace used for melting the metal or alloy, and its temperature is increased very steadily until it is sufficiently high for the ore, metal, or other mixture to be inserted.

Crucibles which are made for sale and for transport over considerable distances must be burned in order to give them sufficient strength. The temperature at which this burning is effected will depend on the purpose for which the crucibles are to be used. The majority of crucibles should not be burned very hard, though the longer they are heated to bright redness the greater will be their durability. If insufficiently heated, the crucibles will be weak and will need more careful treatment during the first heating than is usually bestowed upon them.

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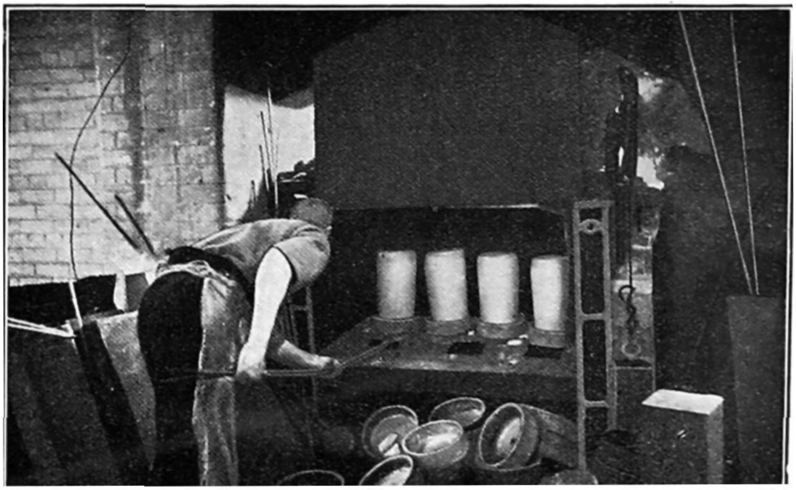
[1] During the "warming through," the crucible should be placed upside down on the fuel, as this reduces its tendency to crack.

Hand-made crucibles for melting steel usually have a hole in the bottom (see fig. 129). This remains open until the crucible and its stand are placed in the steel-melting furnace; a mixture of red and white sand is then thrown into the crucibles and frits, filling up the hole and cementing the crucible to its stand.

Grog crucibles are usually burned in muffle or down-draught kilns at temperatures corresponding to Seger Cones 7 to 12 (1230° C. to 1350° C.), the crucibles being packed one inside another[1] and piled one above the other so as to economise space in the kiln. Some firms burn them on the top of firebricks.

Plumbago crucibles are usually burned at 710° C. to 900° C. (Seger Cones 018 to 010*a*) in muffles or saggars packed with coke-dust or sand, to prevent the undue combustion of the graphite. According to the patent specification published by D. B. Williams and J. R. Stauffer in 1904, the carbon monoxide and other gases evolved in this treatment penetrate the crucibles and convert the clay into a "very refractory substance." It has been found that, contrary to what might be anticipated, graphite crucibles burned at a temperature of 1425° C. in the process of manufacture are not so resistant to oxidation as those burned at a lower temperature. Booze has suggested that this may be due to an increase in the volume of the graphite when it is heated, on account of the extreme pressure under which graphite was probably formed.



(By the courtesy of Messrs. E. Allen & Co., Ltd.)

FIG. 135.—Baking crucibles.

If a plumbago crucible has become reddened by the oxidation of any iron present, it is given a coating of black lead to restore it to its proper colour.

The temperature in the kiln must rise very gradually, particularly at first. For forty-eight hours it should not exceed 110° C., the final temperature being reached after a further forty-eight hours or more.

Care must be taken not to overheat the crucibles, as this tends to make them crack when in use.

Most plumbago or graphite crucibles require to be "annealed" immediately

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[1] This is known as *nesting*.

before use. This is effected by allowing the fire in the furnace, in which the crucible is to be heated, to burn rather low; a supply of fresh coke is then placed on the fire, the crucible is placed mouth downwards in the cold coke, and is surrounded by and covered with more coke. The fire is allowed to burn up slowly until the crucible is red hot, and is then ready for use.

A plumbago crucible is sometimes almost white on the surface; this is due to the carbon having been burned away. This is not serious so long as it is only a superficial action.

Salamander crucibles made by the Morgan Crucible Co. do not require annealing, but can be placed at once on a hot fire.

Graphitised crucibles are made of a mixture of finely divided carbon, such as retort carbon, silica, iron oxide, and a binding material such as tar or molasses. The articles are first baked at a dull red heat and are then packed in granulated coke in an electric resistance furnace. On heating the furnace electrically, its resistance gradually diminishes until it becomes constant, denoting complete change of the carbon into graphite.

Zirconia crucibles are first baked in a gas-fired kiln to harden and make them ready for the final heating in an electric arc furnace. In the latter, the articles are placed on plates of zirconia in order to avoid any reactions taking place between the crucible and its support. The electric furnace is heated fairly rapidly, as the articles have been previously baked and are not susceptible to sudden changes of temperature, and the heating is continued until a temperature of 1700° C. to 2200° C. is reached. This temperature is maintained for a couple of hours or more, according to the size of the articles, as the heating must be continued until all the particles are properly bound together and form a strong, dense body. Zirconia has so low a thermal conductivity that large articles require very prolonged heating before their interior and exterior are at the same temperature. Hence, the duration of heating in the electric furnace must depend largely on the size of the articles with which it is filled.

The nature of the burned product depends to a large extent on that of the furnace gases. At a temperature of 2000° C. it has a characteristic bluish-grey colour, due to the formation of the lower oxide of zirconia, but on heating to a higher temperature a certain amount of zirconium nitro-carbide is formed, giving the ware a reddish-brown colour. At 2400° C. carbon is absorbed, if the atmosphere is sufficiently reducing, the product being a blue-black material very similar in appearance to black marble, extremely hard, and difficult to break. The presence of titanium oxide as an impurity gives the burned product a bluish colour on account of the formation of titanium dioxide at a temperature of 1500° C.

Alumina, mullite, magnesia, thoria, and similar crucibles are burned in the same manner as zirconia crucibles, though the final temperature does not usually exceed 1750° C. and is normally 1500° to 1550° C. Thoria crucibles should not be heated in contact with graphite above 1200° C., or carbides will form.

Scorifiers are burned in the same manner as grog crucibles.

Cooling.—The cooling must be effected very slowly, or a serious loss will occur through the cracking of the goods. The one exception to this rule is zirconia crucibles, which may be allowed to cool rapidly, as they are remarkably insensitive to sudden changes of temperature.

Coating and Lining Crucibles.—In order that crucibles may possess a maximum durability as regards heating and cooling, and also the greatest possible resistance to the corrosion by their contents, it is sometimes desirable to coat them externally or to provide them with an impervious lining. In extreme cases, they may be both coated and lined. For some purposes, there is an obvious advantage to be gained by making crucibles in three distinct layers of different materials, the inner layer being specially suitable for resisting the contents of the crucible, the outer layer being resistant to the abrasion, etc., of the hot fuel, and the centre layer (placed between the others) to give the requisite strength, whilst at the same time being sufficiently porous to resist sudden changes of temperature. By carefully selecting the various materials, the crucibles may be made much more durable than usual, and far less liable to crack when in use. Such triple crucibles are conveniently made by first placing a thin " bat " or sheet of the lining material in the mould and pressing it into position, the correct thickness being obtained by means of a profile. The centre and more porous material is then inserted and shaped up by means of a second profile. Finally, the outer material is applied in a similar manner and the crucible completed. If desired, the order may be reversed, and an outside mould used instead of an inside one.

The slight gloss on clay crucibles is not due to any enamel, but to the fine surface of the material. Occasionally, the makers rinse the crucibles out with a little *glaze* slip made of felspar and whiting—the proportions of each depending on the temperature at which the crucibles are burned—in order to render them quite impervious during the earlier stages of the heating. In most cases, however, users would be well advised not to demand anything in the nature of a glaze, as it only reduces the refractoriness of a crucible when the material in it reaches a melting temperature.

Some manufacturers use a 20 per cent. solution of water-glass or a 10 per cent. solution of soda or common salt in water, or even a bought glaze, probably consisting of lead oxide, flint, and clay, or of Cornish stone, whiting, and flint or clay.

A glaze must usually be applied to zirconia crucibles on account of their excessive porosity, but no wholly satisfactory glaze for this purpose has yet been made on account of the low coefficient of expansion of zirconia. Most of the felspathic glazes craze or shell and so are useless ; a glaze which is free from this defect when fired at 1900° C. to 2000° C., and is quite impervious, is composed of felspar 20 parts, alumina 3, zirconia 12, magnesia 4, and quartz 61 parts ; its chief disadvantage, however, is that it blisters badly and is very unsightly.

Other important coatings and linings are—

Tar, applied by dipping the crucible in molten tar and then burning it under reducing conditions. The tar is thereby decomposed and the pores of the crucible are filled with finely divided carbon.

Varnish, applied with a brush, in order to prevent the crucible from absorbing moisture. Any waterproof varnish may be used. The varnish burns away when the crucible is used.

Refractory linings are made of (i) bauxite, with sufficient fireclay to make it adhere ; (ii) magnesia and calcium borate ; (iii) a more highly refractory clay or other material than that of which the crucible is made, *e.g.* fused alumina, china clay, chromite, plumbago, or various carbides (including carborundum) ; (iv) a mixture of 4 parts of flint and 1 part of fireclay or other suitable proportions (patented by New and Thomas in 1879).

The lining of fireclay crucibles with a mixture of graphite and fireclay was patented by A. Landsberg in 1880. A lining composed of aluminous fireclay, plumbago, and asbestos, with a bond of silicate of soda, was patented by J. C. Waterhouse in 1883.

Magnesia is not suitable for lining fireclay crucibles, as it reacts with the clay, but in 1883 a basic lining composed of baryta, strontia, magnesia, lime, or alumina was patented by T. Egleston. When lining a graphite crucible with magnesia, the crucible is heated to about 140° C. and is painted inside with hot tar so as to fill all the pores. The following mixture is then applied with a flexible knife and is worked until a smooth lining is obtained:—

Sintered magnesia	83 parts
Water	9 „
Water-glass	4 „
Sal ammoniac	4 „

In preparing the mixture, the water and water-glass are mixed together in one vessel, whilst the magnesia and sal ammoniac are mixed in another. The fluid is then added gradually to the solid and stirred until uniform.

Another magnesia mixture which is sometimes used consists of—

Magnesia	2 parts
Fireclay	2 „
Quartz	1 part
Water	2 parts

The proportion of water may be varied according to the consistency of the paste.

A neutral lining of chrome ore and tar, applied hot, was also patented in 1883 by I. Imray.

A lining composed of *sand* bonded with 6 per cent. of *gas tar* was patented by J. B. Sidebottom in 1915.

To preserve crucibles and to prevent them from being damaged by sudden changes in temperature or by absorbed moisture, S. A. Peto, in 1871, patented the external application of a mixture of ball clay 12 parts, Cornish stone 2, grog 4, red clay 1½, and manganese oxide ½ part, the whole being made into a paste with water and applied with a knife. The coated crucibles are burned and then glazed with salt or with an applied glaze.

These linings may be mixed with water or an adhesive solution and applied directly to the crucibles. They may adhere when sufficiently dry or may be fused on to the crucible in an electric furnace or some other form of high temperature kiln. Where the lining material can be fused, it may be applied in a molten state to the crucible, the latter being rapidly rotated so as to distribute the lining by centrifugal force before it has cooled sufficiently to become solid.

A *carborundum coating* may be applied to a fireclay crucible, as suggested by W. Rosenhain, who has recommended a mixture of carborundum with 5 per cent. of china clay (see also Eng. Pat. 219,423—1923).

Zirconia and *zircon* are very useful for coating crucibles in order to increase their durability. The material should be ground to pass through a 150- to 200-mesh sieve, and mixed with an organic binder, the slip being painted on the crucible with a brush, and dried carefully at 150° C. to 200° C. A fresh coating may very usefully be applied each time the crucible is used.

Magnesia crucibles lined with thoria and zirconia successively were patented by C. C. Garrard in 1901.

Crucibles lined with electro-deposited zirconia or thoria were patented by H. Herzfeld in Berlin in 1914.

Carbon liners are sometimes used. They are made of a mixture of equal parts of warm water and treacle, to which sufficient powdered charcoal is added to produce a stiff paste. This is compressed into a clay crucible, and, either then, or after baking, a cavity is cut or turned in the lining, so as to form an interior suitable for a crucible. A lid is placed on the crucible and the latter heated to redness. When cool, the lining can be removed if desired. This process is known as *brasqueing*.

Another method of lining and coating crucibles with carbon was patented by A. & W. Matthews in 1897. It consists in introducing pitch, tar, or oil into the kiln during the burning. These materials are decomposed by the heat and deposit carbon on the contents of the kiln in the form of a strongly adherent film.

The use of a plumbago shell with a clay lining was patented by J. W. Woolford in 1898.

In 1889, C. M. Hall patented a method for lining crucibles with carbon by placing a core within the crucible and filling the intervening space with tar or tar and coke. The mixture is baked with the core in position, the operation of filling being repeated with successively smaller cores until the lining is sufficiently thick.

Wooden crucibles, carefully turned to size, may be placed in clay crucibles and charred before the material to be melted is added. They then make good carbon liners.

Metallic linings may sometimes be used, though few metals are sufficiently resistant to heat. F. G. Keyes, in 1917, patented the use of crucibles lined with tungsten or other refractory metal. A carbon crucible is preferred; the lining is made by spreading a paste of sodium tungstate (or other suitable compound) and an appropriate binder over the inner surface of the crucible, igniting the crucible under reducing conditions so as to liberate the metal and harden it. The lining is then finished by means of a burnishing tool or roller, so as to compress the lining and give to it a firm, tight, and compact surface.

Crucible linings should be of such a nature that they are not attacked by the contents of the crucible. Thus, for aluminium and similar metals alumina may be used as a lining; for calcium, lime and gelatinous alumina may be employed. A good rule is to line the crucibles with the oxide of the metal to be melted in them, borax, silicate of soda, or clay being used as a bond. It is, of course, necessary that this oxide should not have a highly corrosive action on the crucible.

It is sometimes desirable to have the exterior coating of the crucible refractory, whilst the lining is chiefly characterised by its resistance to corrosion. These two characteristics cannot well be procured by the use of a single material, so that the lining and external coating may be of two entirely different substances. In the patent granted, in 1890, to J. B. Alzugaray, the mixtures shown in Table XCII. are particularly specified for crucibles in which the lining and coating are required to possess different characteristics.

There is practically no limit to the materials which can be used as linings and coatings for crucibles.

Properties of Crucibles and Scorifiers.—It is essential that crucibles and scorifiers should be (*a*) sufficiently refractory to withstand any temperature to which they are likely to be exposed, (*b*) unaffected by rapid cooling, (*c*) sufficiently dense to cause no loss of contents by absorption, (*d*) sufficiently resistant to the corrosive action of the contents, particularly metallic oxides, slags, and ashes, (*e*) sufficiently strong to hold the contents safely, *e.g.* a crucible full of steel weighs about half a hundredweight, and it is necessary to carry such crucibles full of molten metal for considerable distances. It is extremely difficult to produce crucibles having all these properties in a high degree, especially when large crucibles are required.

TABLE XCII.—MIXTURES FOR LINING OR COATING CRUCIBLES.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Emery or corundum	70	60	..	..	..	..	..	..
Asbestos	10	10	10	10	..	20	15	20
Graphite or coke	10	30	..	10	60	40	20	..
Bauxite	..	..	80	80	37	..	..	..
China clay	..	..	10	..	..	..	20	..
Fireclay	..	..	..	..	..	..	40	..
Silica	..	..	..	..	..	..	5	..
Magnesite	..	..	..	..	..	..	..	80
Limestone	10	..	..	..	3	40	..	..

The most important property of crucibles and scorifiers is that of durability under trying conditions. The actual "life" or durability of a crucible or scorifier depends quite as much on the manner in which it is used as on the article itself. An inexperienced user may easily spoil each "pot" he handles, particularly if it is a large one, and its weight with the contents is very great and necessitates its being handled very carefully and skilfully.

Briefly stated, the increased life of modern crucibles is due to the discovery of deposits of more refractory graphite and clay, and the incorporation in crucible mixtures of materials shrunk and stabilised in the intense heat of the electric arc. Crucibles made from such ingredients possess increased resistance to external wear by fuel and slags and to internal erosion by fluxes. The earlier attempts to use pure oxides were disappointing owing to the tendency, during use, to develop brittleness, but most of the makers have overcome this difficulty, and the majority of users have now satisfied themselves that these highly refractory crucibles are fully as tough, strong, and resistant to rough handling as the older-fashioned type.

When used several times, clay and graphite crucibles become harder and of a vitreous nature externally. They may then be handled more roughly, but do not bear sudden changes in temperature so well as newer ones. The melter must, therefore, continually look out for signs of their disruption, as a cracked crucible which gives way in the furnace may cause a serious amount of trouble, as well as the actual loss of the contents.

The greatest damage is done to crucibles by the use of unsuitable tongs or by handling the tongs improperly. If they do not fit the crucible properly, or grip it too tightly, they will produce severe strains which rapidly reduce its durability. The heat of the furnace soon causes the tongs to lose their original shape, so that they should be tested frequently against an iron disc turned to a suitable size. This involves very little trouble and greatly increases the life of the crucibles.

Large crucibles should be lifted out of the furnace by some kind of block-tackle, as this strains them less than when men lift them by means of tongs and hand-hooks.

An oxidising atmosphere will burn the graphite from the outside of the pot and weaken it; hence, to ensure the maximum durability of a graphite crucible in any furnace, especially in an oil- or gas-fired one, a reducing atmosphere should be maintained.

Sulphur dioxide from fuels rich in sulphur is highly deleterious to all crucibles.

The higher the temperature at which it is used, the harder the wear on the crucible. In foundries in which alloys of several melting-points are used, crucibles are usually employed first for melting a mixture or an alloy with the highest melting-point and are later used for alloys with lower melting-points. Thus, a crucible might be used for a couple of heats of pure copper, then for phosphor-bronze, then for red brass, next for yellow brass, and, finally, for aluminium. Used in this way, the total tonnage melted per crucible is larger than when each crucible is used exclusively for one alloy. Crucibles are also injured by *packing* them full of cold ingots or scrap, which expand as they are heated to the melting-point; the crucible does not expand as much as the metal, and strains may be set up which crack or weaken the crucible. Crucibles may also be badly injured mechanically by carelessness in poking the fire or in knocking off slag and clinkers.

It must also be remembered that plumbago crucibles are made of different compositions, in accordance with the metals to be melted, the ones made for brass having a short life if used for iron. Very few crucibles used in ordinary furnaces are worn out, but are mainly spoiled by the treatment they receive.

Carelessness in storing crucibles will inevitably spoil them. Even burned crucibles must be kept in a warm place and must be dried very carefully (*i.e.* slowly) before use. It is good practice to stand them on top of the furnace for an hour or two before actually placing them in the fire. A damp crucible will " bump " or crack if put straight into the furnace, and nothing is so annoying as to lose metal owing to a bad or damaged pot. Unburned crucibles need still more care.

If crucibles are not allowed to cool down very much, but are kept hot continuously, so that there is less expansion and contraction, their life is lengthened. This is one reason for the longer life of crucibles in tilting- than in pit-furnaces. The continuous operation of crucible furnaces is unusual, but if the empty crucibles are promptly put back into the furnace and allowed to cool gradually with it, the serious deterioration due to excessive expansion and contraction may be minimised. When once a crucible has been used in a steel works it is never allowed to cool completely until it can no longer be employed. The highest temperature attained by the contents of crucibles used in steel works is about 1500° C. for mild steel and 1650° C. for some alloy steels.

It is clearly impossible to give any accurate figures showing how many times a crucible may be used. Some men can use a crucible eighty times or more for cast iron, whilst others can only use a similar crucible half a dozen times. Similarly with the melting of alloys, steel, and all other purposes for which crucibles are used, the manner in which the tongs fit and the handling of the crucible being much more important than is usually imagined. The following figures represent fair averages:—

For brass, a crucible should serve 70 to 100 times
For bronze, ,, ,, ,, about 50 ,,
For iron, ,, ,, ,, 70 to 90 ,,
For steel, ,, ,, ,, 6 to 10 ,,

For these reasons, no maker can guarantee his crucibles to give any fixed number of melts in any works other than his own.

The *shapes* and *sizes* of crucibles have been mentioned on p. 582 *et seq.*

Crucibles must be made very carefully, so that their walls are of uniform thickness throughout, as, otherwise, strains will be set up which cause cracking or twisting.

The *colour* of crucibles is unimportant and does not, as a rule, give any indication of their value.

The *texture* of crucibles should be as uniform as possible, but the interior of the material should be coarser and more porous than the surfaces. This will enable the crucible to withstand sudden changes in temperature and also the action of slags, etc. The smoother and denser the surface of a crucible, the greater the resistance to fluxes, slags, etc.

Fineness and uniformity of texture are a great protection against corrosion, but these properties are limited by the necessity of avoiding sensitiveness to sudden changes in temperature. Hence, a fine surface and a coarser interior texture is usually best for crucibles.

In an English crucible of great durability, the thin flakes of graphite are parallel to each other and to a tangent to the wall of the crucible, the flakes overlapping each other like tiles on a roof; this arrangement is regarded as highly desirable, as it subjects the graphite to the least oxidation. In crucibles made with Ceylon graphite, the particles are arranged irregularly. Uniformly small particles of graphite are preferable to uniformly larger ones, but if particles of various sizes are used, it is desirable to have an even gradation of particles. The graphite grains should be packed uniformly close together.

Porosity.—A crucible body must be of such porosity as to permit its being drawn from a highly heated furnace, emptied rapidly and then replaced, these actions being repeated as often as necessary. At the same time, the body must be of such density as to prevent thin, fluid fluxes, slags, or molten metals from penetrating into it. By grading the materials as directed in the section on " Preparing the Materials," the desired porosity will be obtained without much difficulty.

Mechanical Strength.—Crucibles must be very strong, especially at the highest temperatures at which they are used, as otherwise they will collapse, and may cause loss of life in addition to other damage.

Crucibles must have great tensile strength so as to withstand the pulling action of the tongs, together with great compressive strength to withstand the pressure of the contents on the walls of the crucible. The latter pressure is often much greater than is generally supposed.

The strength is obtained by the use of a refractory clay which forms sufficient sintered matter to bind the other particles firmly together. It is a well-known fact—though the reason for it has not been explained—that crucibles made of a mixture of three clays are stronger when very hot than those made from a single clay.

The strength of a cold crucible is no criterion of its behaviour when heated. Most Sheffield " teemers " and other users are aware that a crucible is much tougher and stronger at a red heat than when cold, but at still higher temperatures the presence of the molten material makes them weak.

The strength of graphite crucibles depends largely on the temperature to which they have been heated; those which have been kept for some time at a high temperature (1400° C. to 1450° C.) are stronger than those which have never exceeded 1100° C. to 1150° C., and the strength of the harder-fired crucibles is less affected by repeated sudden coolings, such as occur when the crucibles are removed from the furnace.

Refractoriness.—Crucibles must be sufficiently refractory to withstand the temperatures to which they are heated when in use. Except under unusual conditions, the refractoriness of all crucibles is sufficiently great when it is considered apart from their contents and from the action of ash in the fuel used for heating them. When crucibles appear to be insufficiently refractory, the cause will usually be found in the action of the contents on the crucible or in the manner of heating and cooling rather than in the low refractoriness of the materials of which the crucible is made.

There is no definite relationship between the melting-point or refractoriness of a crucible and the highest temperature at which it can be used commercially; so many factors affect its durability. For example, Kanolt[1] states that magnesium oxide heated under reduced pressure (0·5 to 1·0 cm. of mercury) volatilised rapidly at temperatures above 2000° C. Furthermore, if the metal within the crucible is heated by induction, as in a high-frequency induction furnace, the metal is always hotter than the crucible, while if heated in an electrical-resistance furnace or a fuel-fired furnace the crucible is always at least as hot, if not hotter, than the metal inside it. Slight amounts of impurity, and bonding materials, may lower the softening-point of the crucible by several hundred degrees below the melting-point of the pure refractory material.

The increased refractoriness due to graphite is easily shown by heating one test-piece made with graphite and another without it to 1800° C. for several hours; the test-piece without graphite softens and melts much sooner than the other one.

Thoria crucibles are particularly useful at the highest working temperatures, being more refractory than alumina and not affected by heating *in vacuo*, as are magnesia crucibles.

Alumina crucibles are next in refractoriness under general conditions of use.

Spinel crucibles are similar but have a low thermal conductivity.

The following are the maximum safe working temperatures for crucibles made of the materials mentioned; some crucibles made of the same materials, but less pure or with a clay bond, whilst of good quality, may not be so refractory:—

	° C.
Clay, grog, graphite, or plumbago	1700
Sillimanite, mullite, and allied materials	1750
Alumina	1950
Magnesia	2000
Spinel	1900
Silicon carbide	1300
Zirconia[2, 3]	1750
Thoria,[2] beryllia, etc.	2200
Silica (fused)	1300

Crucibles made of thorium oxide can be used at higher temperatures than any others. They are highly resistant to basic materials, but are very sensitive to sudden changes in temperature.

Refractoriness-under-load (p. 356) is of great importance, as if the crucibles are weak when hot they may be burst by the pressure of their contents. It is difficult to determine this property on the crucibles themselves; blocks of

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[1] Kanolt, *U.S. Bur. Stand., Sci. Paper* 212, 1913.

[2] Zirconia and thoria crucibles must be kept out of direct contact with carbon at temperatures above 1200° C.

[3] Zircon crucibles differ from those of zirconia in having a low refractoriness, and they spall badly even when made without any bond.

the same composition and burned under the same conditions are, therefore, used.

The strongest crucibles (when hot) are made of a mixture of zirconia and thoria, but their thermal expansion is very variable and they are very expensive.

Shrinkage.—The shrinkage of crucibles made of clay, graphite and/or grog is usually less than 1½ inches per foot of height, but crucibles made of zirconia, thoria, and similar oxides sometimes shrink as much as one-third of their height. Even when made of highly calcined oxide the burning shrinkage is usually 10 per cent. linear at 1550° C. and 20 per cent. linear at 1750° C.

The shrinkage of all slip-cast crucibles is very high, especially during the drying.

Thermal expansion of crucibles is chiefly important because of its relation to their resistance to sudden changes in temperature. The following figures are significant:—

	Range, ° C.	Cœff. of thermal expansion $\times 10^{-6}$.
Mullite (electrically fused)	20–800	5·4
,, (fine grains)	0–1700	5·3
Alumina (fused)	0–1600	7·7
Corundum (fused)	20–1000	6·0
Magnesia (fused)	20–1000	13·7
Zirconia (electrically fused)	20–800	7·2
Silicon carbide	0–1400	5·0
Thoria (fused)	0–600	93·0

Thermal conductivity of crucibles is very important, as those having a low conductivity require much more fuel to raise a given weight of contents to a given temperature. Most refractory materials, including clay, grog, mullite, and allied materials, have a low thermal conductivity. The addition of plumbago or graphite to clay increases the thermal conductivity so much that only two-thirds of the fuel is required in melting steel in graphite crucibles, and the time required for melting is correspondingly reduced. The addition of sintered alumina or calcium carbide to fireclay, or the use of crucibles made of calcium carbide, has the same effect.

The thermal conductivity of crucibles made of pure fused alumina at 800° C. is 4·9 kg.-cal./m./hour/° C., whilst that of quartz is only 0·72 and of porcelain 0·9. The thermal conductivity of silicon carbide crucibles[1] varies, with the bond, from 0·01 to 0·07 at 400° C. to 0·01 to 0·04 at 1100° C.; the larger the proportion of bond, the lower is the conductivity. The thermal conductivity of recrystallised carbide (without any added bond) is 0·3 to 0·9 at 400° C. gradually falling to 0·3 to 0·6 at 1100° C.

As a result of this high thermal conductivity and a great insensitiveness to sudden changes in temperature, silicon carbide ("carborundum") crucibles reduce the cost of use, and as they pour clean, do not spall and can be used for all ordinary metallurgical purposes, they are increasing rapidly in popularity.

The thermal conductivity of beryllia crucibles is also fairly high, and so makes them relatively cheap to use apart from their high initial cost.

Action of Contents.—The resistance offered by crucibles to the action of their contents is extremely important. No single crucible can withstand the action of all materials which may be heated in it, so that the user should select a crucible which, by virtue of its composition, is most likely to resist those materials which he desires to employ. Thus, a crucible may prove really

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[1] See Baumann and Swentzel, *Bull. Amer. Cer. Soc.*, 1937, **16**, 419–430.

excellent for brass yet unsuitable for iron, and *vice versa*, according to its composition and texture.

A crucible to be used at a comparatively low temperature for a thin, penetrating flux, like lead oxide or borax glass, may be made denser than another crucible which it is intended to use for melting steel at a temperature approaching a white heat. The clay and grog should not be too fine, as too close a texture may lead to excessive solution and corrosion by the flux. From the point of view of resistance to corrosion, vitrified clays are most excellent, but, owing to their density, they cannot withstand sudden changes of temperature without cracking. It is, therefore, necessary to construct crucibles which shall be as dense as possible and yet resist sudden changes of temperature. The increase or diminution of density must be made by regulating the proportion of grog in the clay. This grog is preferably made of the same clay as that used for the crucibles, as too many clays tend to produce a material of lower refractoriness. The duration of the heating also has an important effect on the durability of the crucible, as corrosion becomes much more serious when the heating is prolonged.

Some mixtures are so " corrosive " that even the best crucibles cannot withstand them for long. Thus, the practice of reducing sulphide ores by adding iron nails creates a chemical reaction which is particularly destructive to crucibles. Lead oxide and many other oxides, copper ores, borax, fluxes, and slags all exert a highly corrosive action on the interior of the crucible, and the ash from the fuel used in the furnace often has a similar though less intense effect on the outside of the crucible.

Clay crucibles (with or without grog) have a moderate resistance to corrosion by siliceous slags, but are readily destroyed by basic slags and alkaline materials.

Fused silica crucibles have an extraordinarily great resistance to many chemicals and are extensively used in chemical laboratories. They are inferior in this respect to fused zirconia and fused alumina at temperatures above 1300° C.

Sillimanite, mullite, and similar crucibles resemble clay crucibles in their resistance to chemical attack, but are usually rather more resistant.

Alumina crucibles are more resistant to acids than are the other crucibles just mentioned, but are less so than magnesia crucibles.

Magnesia crucibles are resistant to basic slags, but are soon destroyed by acid ones.

Spinel crucibles resemble those made of magnesia, but have a greater resistance to acid materials.

Silicon carbide (" *carborundum* ") *crucibles* have a high resistance to chemical corrosion, but their uses are limited to those in which no staining of the contents occurs. For metallurgical work this is of no importance, but for some experimental glasses silicon carbide crucibles should not be used.

Zirconia crucibles have a great resistance both to alkaline and acid substances, so that many basic slags and glasses may be maintained at 1750° C. in zirconia crucibles for many hours. Unfortunately, zirconia crucibles are very sensitive to sudden changes in temperature.

Beryllia crucibles have a greater resistance to chemical action than alumina, but magnesia and alumina attack beryllia at high temperatures. Beryllia crucibles are particularly resistant to sudden changes in temperature, but their cost is prohibitive for most purposes. Beryllia crucibles also have a greater resistance to reducing agents than those made of any other oxide. Carbon has no effect on them at any temperature.

Thoria crucibles must not be heated above 1200° to 1300° C. in the presence of carbon. Apart from this, they have a great resistance to chemical attack, particularly that of basic substances.

For methods of testing resistance to corrosion see p. 630.

Resistance to abrasion is chiefly obtained by using only small particles of hard material (silicon carbide or corundum) so as to produce a fine texture, and heating the crucible so that the surface is slightly vitrified or "glazed." This may necessitate the addition of a little flux (*e.g.* borax) to the mixture. The "harder" a crucible the more resistant is it likely to be to abrasion, but resistance to abrasion and refractoriness are, to some extent, incompatible.

Resistance to sudden changes in temperature is an essential property of a good crucible. How necessary is this resistance may be realised from the fact that a crucible may be withdrawn from a furnace at 1800° C., with its contents of 80 lbs. of steel at 1500° C. The steel is at once poured out and replaced by air at a temperature of only 20° C. Yet, notwithstanding the severity of such conditions, crucibles are regularly used for this purpose. On the other hand, many clay crucibles which have been used once and allowed to become cold cannot be used again, as they crack when reheated.

Another instance of the great strain to which some crucibles are exposed is the practice of directing the flame from a gas-burner or lamp on to one side of the crucible. This causes an intense heat on the side exposed to the blast, whilst the other sides remain comparatively cool. Severer treatment than this can hardly be found, and only a few crucibles will stand it.

Crucibles which are too sensitive to sudden changes in temperature probably contain an excess of vitrifiable matter and are too dense in texture. This statement does not apply to porcelain crucibles.

Resistance to sudden changes in temperature is often secured by the addition of graphite, whenever there is no objection to it. A mixture rich in grog or sand also contributes to resistance to sudden variations in temperature, but the product is less refractory than when graphite is used.

Crucibles made of fused silica or of zirconia appear to have the greatest resistance to sudden changes in temperature.

For other information on the properties of crucibles, see pp. 583–595, and the chapters dealing with other articles made of the same materials.

Defects.—The chief defects in crucibles are due to: (i) badly chosen materials, including the mixing of incompatible ones such as magnesia and clay, (ii) improper grading, (iii) unsuitable proportions, (iv) insufficient mixing and sowing, (v) defective pressing, (vi) unsuitable drying, (vii) defective burning, (viii) insufficient annealing, and (ix) faulty storage.

Scalping, flaking, and peeling are due to the material being laminated instead of homogeneous, or to its being too sensitive to sudden changes in temperature. These defects may sometimes be prevented by taking greater care to heat the crucible very gently after placing it in the furnace.

Crucibles rich in silica are improved if they are not allowed to cool below 250° C., because just below this temperature is a critical transition-point from cristobalite to quartz.

Leaks or *cracks*, which allow the molten metal to escape, are chiefly caused by: (i) too rapid heating on first entering the furnace, especially if the crucible is damp, (ii) too rapid cooling after withdrawal from the furnace, (iii) overheating, which makes the crucible "soft" and unable to resist the pressure of the metal, (iv) the contents being "jammed" in the crucible before melting, (v) the contents being dropped carelessly into the crucible, (vi) bad handling with the tongs, (vii) too long a time between leaving the furnace and entering it again, and (viii) exposing a hot crucible to draughts.

Excessive thinning or reduction in wall-thickness by external or internal corrosion and abrasion is usually due to the choice of an unsuitable crucible, to bad fuel or to carelessness in use.

External wear in solid-fuel furnaces is chiefly caused by the reaction between the slaggy ash-content of the fuel and the crucible material, and its amount can, therefore, be minimised by using coke with a low and infusible ash-content and by taking steps to remove ash-accumulations at regular intervals. Oil and gas contain practically no ash, and external erosion is generally negligible when they are employed.

Internal wear is mainly due to the erosion of the crucible by metal oxides or by fluxes used for cleaning the metal; it can be reduced by the addition to the crucible mixings of certain inert refractory oxides manufactured in the electric arc furnace. By such additions, the life of crucibles has been doubled or trebled during the last decade, so that it is now by no means rare to hear of pots giving 100 or even 200 heats of non-ferrous alloys in well-designed furnaces (see " Action of Contents," p. 627, and " Resistance to Abrasion," p. 629).

Testing Crucibles.—A good crucible should pass the following tests:—

(i) When placed inside another crucible and heated to the highest temperature attainable it should not show any signs of fusion. It should seldom have a lesser refractoriness than Seger Cone 30.

(ii) When heated to redness and then plunged into cold water it should not fall to pieces. This test is sufficiently severe to cause cracks in most crucibles, but the cracked portions should not fall apart.

(iii) The crucible is half-filled with litharge or red lead, and heated for five minutes after the contents are completely fused. When cold, the crucible is broken and examined. The amount of corrosion should not be serious. This test may be modified by using other fluxes according to the purpose for which the crucible is used, as in Orton and Henderson's test (*below*), where soda is added to the lead compound.

A common test for the ability of a crucible to withstand corrosion is to half-fill it with copper and to add a little borax. As the copper melts, part of it will be oxidised, the borax will absorb the oxide and will rapidly corrode the crucible, unless the latter is of excellent quality.

Another useful test consists in melting litharge and soda (1 : 2) in the crucible to be tested. Most crucibles will be perforated by the fused mixture after a few minutes' heating, but a satisfactory crucible will stand prolonged heating. E. Orton, jun., and B. Henderson consider that the value of a crucible may be best determined: (1) by the proportion of crucibles from the whole number tested (at least six of each kind being used) which can stand two treatments with the flux before being perforated, (2) by the relative losses in weight of the crucibles due to the absorption of the clay by the slag, and (3) by the character of the corrosion, whether it is smooth and uniform or pitted and rough. They found that crucibles made of aluminous clay were perforated more rapidly by the litharge-soda mixture than those crucibles made of coarse particles of silica, though the latter are more readily attacked as a whole by the flux, the attack being of a general character and little perforation occurring. Siliceous crucibles are disadvantageous when cast iron is being melted, as the molten metal absorbs silicon from the crucible.

IMPROVISED CRUCIBLES.

When properly made crucibles cannot be obtained, as in prospecting and in rough smelting in out-of-the-way places, rough ones may be improvised thus:—

(i) Crucibles made of Portland cement mixed with water to form a soft paste, moulded, and then dressed before the cement has set too hard, are sometimes used. They are inferior to crucibles made of fireclay. Crucibles made of Portland cement should not be more than 2 inches wide, 3 inches deep, with walls $\frac{1}{8}$ inch (or preferably $\frac{1}{16}$ inch) thick.

(ii) White or blue clay may be mixed into a stiff paste with water, shaped roughly by hand, and the rough crucible may be allowed to dry and then gently heated over a fire until it is partly baked. It may then be burned in the fire and raised to a red heat for several hours.

(iii) Where it is desired to melt a metal, it is sometimes preferable to add a flux to the clay used. Wood ashes are generally regarded as the most suitable in out-of-the-way places, but a little table salt may also be added if desired. A mixture which has been largely used for many years by prospectors consists of equal parts of wood ashes and dried white or blue clay. The materials are crushed to powder, mixed thoroughly in the dry state, and then with water to form a moderately soft paste, which can be roughly shaped by hand and then allowed to stiffen. When sufficiently stiff, it may be trimmed with a knife. The crucible is then allowed to dry, and is afterwards heated slowly to bright redness, retained at a red heat for several hours, and either used at once or allowed to cool whilst covered with hot ashes.

UNBURNED CRUCIBLES.

Crucibles made of *plaster of Paris* are sometimes used for experimental purposes when others are not available. A mould is made by coiling a long strip of cartridge paper or a shorter strip of linoleum around a test-tube, round ruler or other object of the same diameter as the desired crucible, and then tying the coil with string. A sheet of stout paper is then pasted over the end of the casing, in much the same way as a jam-jar is covered; the core is then removed. Plaster of Paris is made into a thick fluid and is placed inside the mould by means of a spoon, the interior of the crucible being shaped by means of the back and handle of the spoon. When the plaster is set, but before it is too hard, the casing is removed and the outside of the crucible is trimmed to the desired shape with a knife. The mould should be dried and warmed before use.

According to an anonymous German author[1] satisfactory crucibles for copper-nickel alloys in high-frequency induction furnaces may be made of natural sand 33, ground sand 30, coarse quartz 10, powdered glass 15, and clay 12 parts. The materials are mixed with 6 to 7 per cent. of water, shaped in a press and dried for 30 hours before use but not burned. The "inventor" of this recipe claims that in the first time of use the crucible is sufficiently sintered to prevent fracture in subsequent use. The use of unburned linings for induction furnaces is increasing (see p. 487).

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[1] *Feuerfest*, 1933, 9, 157.

CHAPTER XIII.

GLASS-HOUSE POTS AND TANKS.

THE highly refractory vessels used in the manufacture of glass are known respectively as *glass tanks* and *glass pots* or *glass-house pots.*

Glass tanks (fig. 136) are of the nature of the hearth in a reverberatory furnace. If small, they may be made in one piece, like a glass pot, but are more usually built of slabs, bricks, or blocks of refractory material. The nature of the materials will be readily understood from a study of the properties required for glass pots in the present chapter and of the manufacture and properties of fireclay bricks (Chapter II.) and blocks (Chapter IX.). Well-made tank blocks should have the following characteristics: (*a*) they should not shrink or expand seriously when in use; (*b*) when drilled or broken, the blocks should be free from black cores, which would show a lack of control during the burning; (*c*) they should ring clearly when struck; (*d*) they should not vary seriously in size from the required dimensions—a variation of $\frac{1}{8}$ inch in each dimension may be regarded as reasonable in blocks which have not been ground to size;[1] (*e*) they should not be too porous—about 25 per cent. by volume of porosity may usually be regarded as a maximum; and (*f*) the volume-weight should not be less than 143 lbs. per cubic foot, or 13¼ ounces per cubic inch.

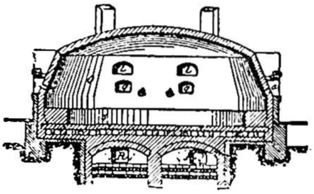

FIG. 136.—Section of glass tank.

Glass pots (figs. 137 to 139) are really large crucibles of special shape. They are of two chief types: (*a*) *open*, as in fig. 137, and (*b*) *covered*, as in fig. 139. Open glass pots are used for the production of leadless glasses (plate glass, blown glass, etc.). Covered pots are used for glasses containing lead compounds (flint glass, crystal glass, strass, etc.), in order that they may be protected from dust and from particles of fuel which might fall into the pot, reduce the lead compounds, and so spoil the glass. Covered pots are also used for optical and other glasses where it is highly important to keep out all particles of dust, etc. They are usually provided with a partially covered opening at the front, through which they are filled and emptied.

Covered glass pots are of various shapes. Some have partitions (fig. 140), so as to keep floating material from being withdrawn along with the molten glass.

Most of the glass pots used in the United Kingdom are of the covered

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[1] From the user's point of view, the maximum variation in any dimension should not exceed 1 per cent., but this can only be secured by grinding or rubbing the finished blocks until they are exactly the size required.

form shown in fig. 139, open pots (figs. 137, 138) being seldom employed in this country except for the commoner glasses.

The shapes of glass pots depend somewhat on their size, all large pots being circular. Square pots are used in some works; they present a larger heating surface and so save a little fuel. Pots of oval section have a similar advantage, but tend to collapse when full of molten glass. Oval pots should not be used for the less fusible glasses, but are advantageous for those which melt at a low temperature. Circular pots are best for most purposes.

One of the most popular shapes of glass pot is a frustrum of a cone (fig. 137). It has several advantages over cylindrical pots, including—

(1) More rapid drying during construction.

(2) More effective tamping during construction.

(3) More effective heating when in use, as the heat plays around the lower part of the sides, whereas when a number of cylindrical pots are placed close together, the heat is largely confined to the bottom of each.

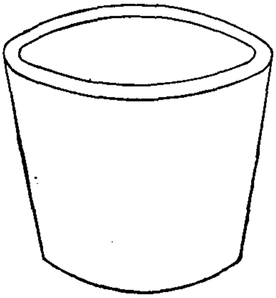
FIG. 137.—Open glass pot.

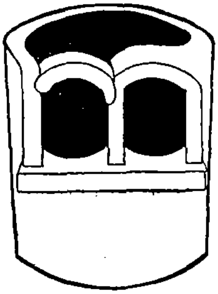
FIG. 138.—Open glass pot.[1]

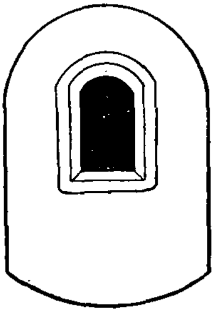
FIG. 139.—Covered glass pot.

Glass pots should be wide and short, rather than narrow and tall, as the former shape is more convenient to the glass maker; it is heated more rapidly and is more durable.

Covered pots for continuous work are employed where the output is sufficiently large and regular and the nature of the glass permits their use. They reduce the cost of making the glass, permit a more effective use of the fuel, and the pots last longer. Their great drawback is that the glass is not readily accessible and does not clarify so well, but for some purposes this is unimportant. Some of the covered pots have two or more separate divisions, as in fig. 140, in which A is the melting pot proper, the molten glass flowing through an aperture *a* at the base of the partition into the chamber B, from which the glass is withdrawn on a blowpipe inserted through *b*. The clearing chamber B has about two-thirds of the capacity of the melting chamber A. It is preferable to have the aperture *a* near the back of the pot, as when it is placed in the centre of the partition the glass does not clear so readily.

Siemens' glass pot (fig. 141) effects a better clearing of the glass, especially if the lower end of the pipe is partially closed and the pipe is filled with porcelain balls, as in M. Epstein's patent (1891).

The *sizes* of glass pots vary greatly. In England, they are of various

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[1] In 1904, F. Lang patented a glass pot similar to that shown in fig. 138, arranged for continuous use by inserting a movable tube of fireclay into one of the mouths and withdrawing glass through this, fresh material being fed in through the other mouth.

diameters up to 6 feet; in France, Germany, and the Netherlands pots more than 3 feet in diameter and 3 feet high are seldom used.

The pots used for plate glass are the largest, and range from 4 feet to 6 feet in diameter and 2 feet 6 inches to 3 feet high. Those for bottle glass are 3 feet to 4 feet in diameter and 2 feet to 3 feet high. For pressed glass, rather small pots, and for hollow ware, optical and other special glasses, pots 14 inches to 40 inches in diameter are used.

It should be noted that pots must be much larger than the volume of the glass they are intended to contain, the effective capacity being only about three-quarters of their calculated capacity. Thus, a pot with a capacity of 7 cubic feet will hold about 100 lbs. of glass.

In small and medium pots the height and upper diameter are usually equal, but large pots are generally wider than they are high. The thickness of the bottom of the pot is usually one-twelfth of the greatest diameter, and the thickness of the walls one-twentieth of the greatest diameter.

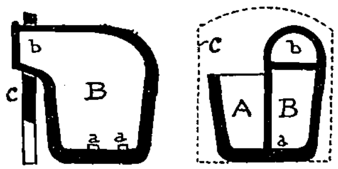

FIG. 140.—Covered glass pot with partitions.

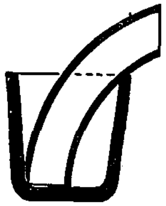

FIG. 141.—Siemens' glass pot.

Some manufacturers prefer the thickness of the walls to be three-quarters that of the bottom, and the product of the thickness of the bottom and walls to be one-hundredth of the height, multiplied by the diameter of the pot. Thus, if W=thickness of wall, B=thickness of bottom, H=height of pot, and D=greatest diameter of pot, then

$$W \times B = \frac{H \times D}{100}.$$

The problems which confront the manufacturer of glass pots are different in many ways from those involved in the manufacture of refractory bricks and crucibles. In glass furnaces, the maximum temperature reached seldom exceeds 1400° C. to 1500° C.—a temperature which even second-grade refractory materials will withstand quite satisfactorily under oxidising conditions. With skilled management, the changes in temperature are by no means so rapid as in furnaces used for melting metals, so that in this respect also the conditions are comparatively simple, spalling, crumbling, and other defects due to sudden changes of temperature being seldom seen. On the other hand, it is essential that the glass, or the materials from which it is made, should not be spoiled by absorbing any material from the pot or tank-blocks, and this is a restriction which is extremely difficult to enforce. The difficulty from the glass manufacturer's point of view has been well expressed by Rosenhain, who suggested that the chief difficulty in the manufacture lies in the pots, which are "costly and slow to make, breakages are frequent, and each pot can only be used once for optical glass. The glass dissolves iron compounds from the clay used in the pots, and the stirring cannot be carried out thoroughly, or the sticky matter adhering to the sides of the pot would be worked into the glass and would spoil it." As even the best clay available is attacked by glass, he considers that it will be necessary to seek for some other material of which to make the pots, and the National Physical Laboratory is experimenting in this direction. Among suggested materials are magnesia, silundum, carborundum, tungsten, molybdenum, etc., but at present it seems exceedingly doubtful whether any substance other than fireclay or fused silica possesses all the requisite properties.

In consequence of the difficulty of drying large pots, a manufacturer is often in a difficulty, particularly as they are frequently taken to the glass-works in a dried condition, in which they greatly resemble vessels of dried mud, and are, consequently, very fragile.

The greatest possible care is required in the manufacture of glass pots so that they may withstand the chemical action of the glass-forming materials, the great pressure of the glass on the sides of the pots, the high temperature to which the pots are exposed, and the frequent changes in temperature to which they are subjected. If the density, mechanical strength, or refractoriness is too low, serious difficulties will occur when the pots are in use, and irretrievable damage may ensue. The loss to the glass manufacturers which may be caused by what the maker may regard as an insignificant defect in a glass pot is often so serious, that the saving of a few shillings in the cost of making the pots is not a matter which most glass manufacturers will consider.

Materials.—Most commercial glasses are so siliceous that they may be regarded as acid in character, and, therefore, the vessels in which such glasses are melted must also be acid in character; basic materials would be very rapidly attacked by the molten glass and the latter would be spoiled. For instance, sintered magnesia is useless, as it rapidly combines with the silica in the glass mixture, and the pot or tank soon collapses. On the other hand, there is sufficient alkali and base in most glasses to make it undesirable to keep them too long in contact with highly siliceous materials, as these are also disintegrated though not very rapidly.

On the whole, the most suitable materials for making glass-tank blocks and glass-house pots are the siliceous rocks and clays occurring chiefly in the Carboniferous beds. The properties required in the materials used for making glass pots are not all the same as for glass-tank blocks; for the pots, the materials must be plastic in order that the walls of the pots shall not be too thick to permit the heat required to melt the glass to pass through them, but the materials for tank blocks need not be so plastic, and the thickness of the blocks is of no consequence, as the heat is applied direct to the glass and not through the walls of the furnace.

Glass pots are made of mixtures of clay and grog. The *clays* used for the purpose in Great Britain are almost invariably the best qualities of Stourbridge and Scotch fireclays. The clay most extensively used for glass pots in Great Britain is mined at Stourbridge at some distance below the coal.[1] It has a softening-point corresponding to Seger Cones 32 to 33. Special parts of the seam are selected for the purpose, and a large proportion of the material actually used is in the possession of so few firms that few details concerning it are available for publication. In his capacity as technical adviser, the author has a considerable amount of information in his possession, but the interests of his clients prevent some of this being made public at present. In other districts, materials suitable for glass pots and tanks occur at Mexborough and Wickersley, near Rotherham, in the Stannington Black Bed or Pot clay,

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[1] See analysis in Table XI. Highly siliceous clays, and especially those which contain free silica, are undesirable. All clays must be fully weathered.

the beds between the Clay coal, and the Halifax Hard Bed ganister near Deepcar, and in selected parts of the Lancashire beds. China clay from Cornwall and Devonshire, and other kaolins, are also used in admixture with alumina.

Aluminous fireclays are, in general, more resistant to corrosion by glass-making materials, but their shrinkage when in use and their low mechanical strength at 1300° to 1450° C. are objectionable. When a pot made of highly aluminous clay is corroded, the loosened product makes the molten glass viscous and "stringy" and very difficult to fine. Aluminous clay, of course, may also produce "stones" in the glass. Fine aluminous clays are, on the contrary, superior to siliceous clays. A high alumina-content increases the resistance of glass-house pots to corrosion, but only if the alumina has been converted into mullite; otherwise the alumina tends to form "stones" and spoil the glass.[1]

Siliceous fireclays shrink less in use, and pots made of them are stronger at high temperatures, than those made of aluminous clays. If coarse particles of quartz are present, however, siliceous clays should not be used. Fireclays containing 60 to 70 per cent. of silica and 20 to 25 per cent. of alumina are usually the best for glass-house pots, provided the drying shrinkage is not more than 5 per cent. linear and the burning shrinkage is not more than 1·5 per cent. linear. Such clays, when mixed with about 40 per cent. of grog of the same composition, often produce better pots than highly aluminous clays with aluminous grog.

The grog should be made of the same clays, fired at Seger Cone 8 (1250° C.), and then ground so that all passes through a 12-mesh sieve and half of it through a 30-mesh sieve. The grog "dust" should, usually, be removed before use.

No mixtures of bauxite and clay should be used, as these produce highly "stringy" glass.

The use of clayey slate or of slate débris has been tried, but the siliceous cement is too soluble in the molten glass, and leaves loose grains of indurated clay which float about in the glass and spoil it. The flaky nature of the slate is also objectionable, as glass-melting pots should be made of nearly spherical particles.

For further information on the localities in which fireclay and other suitable materials occur, see Chapter I.

Many British manufacturers of glass pots use only one clay (though most of them use clay from several parts of the same deposit), but this simple procedure is seldom possible in other countries, and there it is generally necessary to use two, three, or even four kinds of clay. In the United States, a mixture of German (Gross Almerode) clay and American pottery clay was formerly used, but American glass-pot manufacturers now claim that they have found an efficient American substitute for the German clay.

The superiority of the plastic[2] Gross Almerode clay is chiefly due to the ease with which it disintegrates in water, and the remarkable uniformity with which the water distributes itself through the mass. Most other available clays become soft externally when soaked, but the core of each piece remains hard for a long time. Gross Almerode clay has also a low shrinkage, a very high binding power, and a high refractoriness.

The European clays which bear the closest resemblance to Gross Almerode clay are found in Belgium.

[1] Partridge, *J. Soc. Glass Tech.*, 1930, **14**, 63.

[2] Gross Almerode clay occurs in alternate layers of lean and plastic clay, and care should be taken to use only the plastic clay for glass pots.

When a glass pot of the very highest attainable quality is to be made, it is found that a fireclay or china clay (kaolin), when alone, produces, on burning, a porous mass, which would soon be decomposed and corroded by the glass mixture. A vitrifiable (ball) clay, which burns to a dense impermeable mass, is not appreciably corroded, but it cannot be used alone, as it is not sufficiently refractory and is too sensitive to sudden changes in temperature. A vitrifiable plastic clay, such as some ball clays, is, however, of great value in binding together the particles of less plastic material. For this purpose, the clay should be highly plastic, so that only a comparatively small quantity is required to make the pot sufficiently strong in the raw state to bear transport before firing. Such a binding clay should vitrify at a sufficiently low temperature, but it must not be overfired at the highest temperature to be reached when the pot is in actual use.

For these reasons, it is generally best to use two clays and grog. The *base clay* should be highly refractory and as pure as practicable; it may be highly aluminous or siliceous. The *binding clay* should have a high binding power and a low vitrifying point; usually a ball clay is best for this purpose.

The percentage of iron oxide in the materials of which the pots are made does not, in most cases, need very serious consideration, as with fireclays, ball clays, and china clay of good quality, the amount of iron abstracted and included in ordinary glass during the melting is not usually sufficient to spoil it. In the case of optical glass, however, the presence of iron is more serious, and, as it is usually impossible to secure clays, etc., wholly free from iron, the pots may be made of the best available materials and afterwards treated so as to remove the iron compounds. A method suggested for this purpose by Hostetter, Roberts, and Ferguson consists in passing chlorine gas (from a cylinder of liquid chlorine) into the red-hot pot. This forms a volatile iron chloride, so that most of the iron on the interior surface of the pot, and all that is likely to contaminate the glass, is removed at a cost of only six to ten shillings per pot. Y. Ichikawa,[1] on the contrary, found that on heating a clay, containing 3·13 per cent. of iron as ferric oxide, with charcoal in a current of dry chlorine gas at 100° C. to 150° C. for two hours, only half the iron was removed.

In America, attempts have been made to improve the quality of glass-house pots by avoiding the use of fireclay and employing purer materials. The best results have been produced with *porcelain pots*, which are more satisfactory for making optical glass, as they are denser, more uniform, have a lower iron content, and when attacked by the glass they do less harm to the latter. J. W. Wright and D. H. Fuller recommend the following limits of composition for porcelain glass-house pots:—

Ball clay	17–22 per cent.
China clay	27–28 „
White biscuit grog	48 „
Felspar	6·5–7·0 „

Porcelain pots made in the United States in recent years have been made of:—

Plastic clays	24–32 per cent.
Kaolins	12–15 „
Broken glass-house pots . . .	15–20 „
Felspar	8–10 „
White ware biscuit or flint or both .	20–40 „

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[1] *Journ. Chem. Ind.* (*Japan*), 1920, 25, 1310.

The slip-casting process is used, 0·02 per cent. of a mixture of equal parts of sodium carbonate and sodium silicate being used as the electrolyte, and the slip having a sp. gr. of 1·98.

Montgomery and Scott[1] give the following limits of composition:—

TABLE XCIII.—ANALYSES OF PORCELAIN GLASS-HOUSE POTS.

	High Silica Type.	Low Silica Type.
Silica	74·05	60·05
Alumina	19·14	31·70
Iron oxide	1·66	2·11
Titanium oxide	1·00	0·40
Lime	0·19	0·34
Magnesia	0·22	0·50
Potash and soda	0·44	0·40
Loss on ignition	4·30	4·50

The composition which is most likely to secure the best results is that of the hard paste porcelain, which has for so many years been used for the construction of crucibles, and other apparatus used in chemical laboratories, and described in Chapter XVI.

The porosity of porcelain glass pots varies from about 2·6 at the rim to 6·4 at the bottom, whilst fireclay pots vary from 9 to about 20 per cent. The porcelain pots have also a rather lower apparent specific gravity, viz. 2 to 2·3 as against 2·3 to 2·6 for fireclay pots. Porcelain pots are not so easily corroded as fireclay pots, especially with glasses rich in barium oxide and lead oxide, which readily penetrate a fireclay pot. Porcelain pots are, however, rather less refractory and rather more brittle than fireclay ones, though they possess ample strength for making optical glass, and for other glasses they can be used repeatedly.

To test the suitability of several clays for the manufacture of glass pots, it is desirable to make each clay into a crucible and to fuse a quantity of glass mixture in it. The clay which is least acted upon by the glass will probably be the best for the purpose. Another method is to mix each of the clays with one-half its weight of ground glass and to determine the fusion-point of the mixture. That with the highest melting-point will probably contain the best clay for glass pots. Neither of these tests is of great reliability, but they serve to sort out the majority of unsuitable clays. An analysis and a test of the refractoriness of the clay will also prove useful, but physical tests are usually of greater value than chemical analysis.

The ideal clay for glass pots is one which is plastic, very refractory, and yet burns dense at a moderate temperature. Its refractoriness should not be below Seger Cone 30. Such a clay would probably crack and spall if used alone, but the addition of a suitable proportion of grog entirely overcomes this defect. The conditions under which glass pots are used are, however, so very severe that only few clays are suitable, and no single clay can be regarded as "ideal." The principal properties required are—

(1) Low drying shrinkage.
(2) High tensile strength when dry (permitting safe transport).
(3) Low burning shrinkage.

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[1] *Glass Industry*, 1922, **3**, **91**.

(4) Porosity sufficient to ensure resistance to changes in temperature to which the pot will be exposed, but not so high as to enable the glass to corrode the pot readily.

(5) High refractoriness under load.

The clays must have been fully weathered, for many pots are spoiled merely because they are made of " raw " and immature clays!

For methods of purifying clays see p. 256.

The *grog* may be burned specially at Seger Cone 14 to 16, but it is more usual to employ a grog made by crushing damaged but unused glass pots. The use of broken glass pots from the glass works is seldom satisfactory, though some manufacturers buy back waste pots and use these over again in the ground state. It is generally found, however, that the long exposure to heat effects changes in the material, which render it undesirable to have a large proportion of broken pot in new ones, and the risk of including fragments of glass and other readily fusible matter is also very great. It is particularly important to avoid all pieces of pot which have a glassy fracture, as these will reduce the heat resistance of the new pots. In any case, the grog must be highly refractory and burned very hard, but not to vitrification.

Some of the oldest and most experienced pot-makers have long maintained that the grog and binding clay should both be made from the same clay, but this is not essential and in many instances is not satisfactory. The grog should be made of one or more refractory clays (*i.e.* base clays, p. 637), and should not usually contain any vitrifiable clay. There are obvious advantages to be gained by purifying the clay before making it into grog, but this is seldom done. Specially prepared grog is preferable to other materials because a harder, denser, and more angular material than ground saggars, firebricks, or old glass pots can be produced, and the clays from which it is made can be selected solely with a view to producing a suitable grog. Grog made of white-ware biscuit has been recommended for making pots for optical glass by J. W. Wright and D. H. Fuller and others. They suggest that such grog should be of different sizes in order to secure a dense mass. Four grades are preferable, consisting of 30 per cent. retained between 10- and 20-mesh, 40 per cent. between 20- and 40-mesh, 17 per cent. between 40- and 80-mesh, and 13 per cent. passing through 80-mesh. P. Marson has strongly recommended that more of the grog should be coarser than 10-mesh, and that it should not leave a residue of more than 35 per cent. on a 16-mesh screen. There are advantages to be gained by using no grog of less than 50-mesh, but this is seldom separated.

Usually, fine grog is not highly objectionable in glass-house pots; it produces vessels of great mechanical strength and with a smooth compact surface, though care should be taken to avoid an excess of fine grog, as it makes the pots too sensitive to changes in temperature. German makers do not remove the dust from the grog, as this dust reduces the shrinkage, and the finest grog also forms a dense non-porous body very suitable for glass pots. The coarser grog acts as a skeleton, and renders the pot insensitive to temperature changes but not resistant to corrosion.

It is important that the particles of grog should be as uniform in size as practicable, otherwise " seeds " or " stones " will be produced in the glass. If possible, the particles should be angular and not rounded. The grog should be free from pieces of fused material and from black core. It should have been burned at 1450° C., or above; under-burned grog is a cause of cracks and other defects in the pots. For further information respecting the manufacture of grog see p. 141.

Quartz should not be used in the manufacture of glass-house pots, and clays which contain large (0·12 inch) pieces of free quartz should as far as practicable be avoided. Such quartz is readily dissolved by the glass, and leaves hollows in the pot which offer an increased surface for corrosion.

Fused alumina instead of grog has been patented (Eng. Pat. 375,806), but it is very liable to produce " stones " of a particularly objectionable type. The use of fused alumina in electro-cast blocks (p. 511) is free from this objection, which only applies to pieces of alumina mixed with a binding clay.

Sillimanite (the commercial name for calcined cyanite) has given excellent results in tank blocks, but not as a substitute for grog in glass-house pots. Better results have been obtained when sillimanite was used for slip-cast pots composed of 80 per cent. of sillimanite and 20 per cent. of clay.

Further research on sillimanite is desirable, as it has a small corrodibility, great resistance to sudden changes of temperature, and a very high refractoriness. Further information on natural and artificial sillimanite will be found in the section on " Sillimanite " in Chapter I. and in the section on " Sillimanite Bricks " in Chapter II.

The use of *graphite* in the paste increases the resistance of the glass pots to corrosion, but some makers complain that it stains the glass.

Magnesium aluminate (*spinel*) appears to be unsuitable for glass-house pots as the pots are too permeable to molten glass.[1]

Preparing the Materials.—The clays and grog should be carefully examined and all obvious impurities picked out, as even a small proportion of impurity greatly affects the durability of the pots. The picked materials are then *weathered* and should, afterwards, be crushed, *dried*,[2] and ground.

The grinding of the clay is effected by any of the ordinary grinding machines, edge-runner mills being the most generally used, though there is reason to believe that a tube mill might give more uniform results and would not cause the loss of so much flour of clay. There is a considerable diversity of opinion as to the most suitable size of the clay particles for use in glass pots; some makers contend that the finer the clay the better, whilst others prefer a considerable proportion of coarse particles. A generally accepted mesh for the clay sieve has 15 or 16 holes per running inch, so that the coarsest particles will be about one-thirtieth of an inch in diameter. Coarser particles than these are certainly undesirable in the clay, though often present in it.

The clay must be sifted carefully. This sifting is much easier if the clay is dried, either before or after grinding. Some firms prefer to dry the coarse material, but others usually grind it in a slightly moist condition—so as to avoid the clouds of dust which are otherwise formed in the mill-house—and then to dry the material (if necessary) before sifting it. In Great Britain, the raw clay is very seldom dried, it being the custom to disregard the water it contains; yet the greater regularity with which a dry powder can be sifted and the greater accuracy possible in proportioning it are certainly in favour of using a dry material.

The *grog* should be graded, and should not contain particles larger than those indicated on p. 639.

Further information on the crushing of clays and grog is given on pp. 143 and 261.

Proportions.—The proportions of each kind of clay and grog which are

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[1] Parmlee and Lyon, *J. Amer. Cer. Soc.*, 1935, **18**, 338.

[2] The drying is very important in order to ensure correct proportions of each material being used.

most suitably used in the manufacture of glass pots must be decided as the result of experience and trial, as so much depends on the plasticity and binding power of the clays used. They should be such as to produce the desirable properties mentioned on p. 656.

A highly plastic clay with very little grog is easy to work, and, though it has a heavy shrinkage in drying and burning, it produces pots of great strength and toughness, which are highly resistant both to heat and corrosion. The difficulty experienced in using such a mixture is in the drying and burning stages, when minute cracks—often too small to be discernible—are produced and cause the pot to fail in use. If the greatest possible care is taken, the proportion of failures may be very few, but as they are nearly all discovered by the user and not by the manufacturer, they lead to trouble and make it difficult to obtain repeat orders. A very lean mixture, on the contrary, will shrink very little in drying and burning, and therefore will be free from shrinkage cracks, but pots made of such a mixture would be exceedingly tender and difficult to handle. If, however, they can be set in the glass furnace without damaging them, they will form strong pots which are much more durable and less sensitive than those made of a more plastic mixture. The advantage of a lean mixture is that nearly all the defective pots are discovered before they leave the works, so that they have a better reputation among buyers, because there is a much smaller proportion of failures during use.

The glass-pot maker must endeavour to use such a mixture of grog, lean and plastic clays, as will give him most, if not all, the advantages of both lean and plastic mixtures, and his success will largely depend on his ability in this direction. It is wise to err on the side of leanness for the reason mentioned above. In some cases, *e.g.* in the manufacture of plate glass, the pot with its contents is lifted out of the furnace and carried by a crane to the casting shop, where its contents are discharged on to a large table. The sudden change in temperature from a white-hot furnace to a cool shed is so trying that only those pots which are made of a lean, coarse mixture, producing a porous pot with a more compact inner surface, can be used satisfactorily.

Bearing the foregoing limitations in mind, it will be found that many glass pots are made of almost equal parts of clay and grog, though another well-known mixture consists of—

Stourbridge clay	8 parts
Grog from same	5 ,,
Old glass pots	5 ,,

Some glass-pot manufacturers work with so lean a fireclay that they can only add one-fourth of its weight of grog, but if the clay is suitable in other respects, this small proportion of grog may prove quite satisfactory. As a general rule, however, 50 per cent. of grog is desirable if the clay is sufficiently strong to bind this proportion of grog into a strong mass. The Refractories Committee of the Society of Glass Technology, in 1918, published a suggested specification for glass pots consisting of three clays, viz., grog, a base clay or refractory clay, and a binding clay. This specification has not been widely accepted on account of the number of technical objections raised to it.

When graphite is used, the proportions found to be suitable in some works are—

	A.	B.
Graphite	4	3 parts
Clay	2	1 ,,
Grog	1	0 ,,

All the materials must pass through a sieve with 5 to 10 holes per running inch, but the clay should pass completely through a sieve with 16 to 20 holes per running inch. The best clays, when made into a slip with water, will leave very little residue on a 200-mesh sieve.

The composition of the pots should depend on the kind of glass to be produced. For " common " soda-lime-silica glass, about 25 per cent. of grog may be used, and the fired pot should contain 24 to 27 per cent. of alumina, but less than 2 to 5 per cent. of iron oxide. For glasses rich in lead (flint glass), siliceous pots containing not more than 10 per cent. of grog are preferable; they should not contain more than 23 per cent. of alumina and should be as dense as practicable. If much alumina is present, the glass will tend to be viscous and cordy, and if the pot is porous and rich in grog there will be an undue proportion of " stones " in the glass.

Mixing.—It is in the mixing and subsequent treatment of the materials, even more than in their composition or precise proportions, that the success or failure of pot-making lies, for the most perfectly proportioned materials will form defective pots if the mixing is not sufficiently thorough or if the after-care of the pots is insufficient.

It is highly important that the materials should be mixed uniformly, and this requires very thorough treatment. On the Continent, it is considered necessary to place all the dry materials in a rotary mixing drum or in a trough 6 feet by 18 inches by 18 inches, and to mix them in this until a uniform mixture is produced. The contents of the drum or trough are discharged into a trough mixer and treated with sufficient water to make a stiff paste, which is allowed to sour for twenty-four hours. It is then cut into thin horizontal slabs with a wooden spade, and these slabs or bats are thrown with great force into another trough. This cutting and throwing (sometimes known as *wedging*) is repeated once or twice each week for a couple of months, so as to produce a compact and completely homogeneous paste. This paste is then allowed to rest for a fortnight, during which time it is covered with wet cloths. Concrete mixers and other rotating drums are not really suitable for mixing raw clay and grog, as their rolling action separates the particles according to size.

In British and American works, the following process is one generally recognised as the most suitable for obtaining a good mixture: The materials are measured separately, and are then sifted on to each other on the floor, so as to form layers on one another. This sifting is necessary to keep out any accidental lumps of material and also to secure the uniformity of the layers. The dry materials are then mixed together with the aid of wooden rakes without teeth, so as to make the product as uniform as this method of mixing permits. The heap is then wetted with hot water [1] and is trodden by men with bare feet (figs. 127, 142) until a uniform paste is obtained. A mixer or pug mill may be used, though the more primitive process of treading is considered to be better. The treaders must do their work with skill and thoroughness, and usually work the material six or eight different times with their feet before it is considered well mixed. Too much water must be avoided, as it tends to cause cracks in the pots. It is a great temptation to the treaders to use too much water, because it makes their work so much less tiring.

Between each "treading" the paste is carefully stored for one or more weeks in order that it may "sour," after which it is again mixed and again set aside to sour.[2] This treatment is repeated as often as is considered neces-

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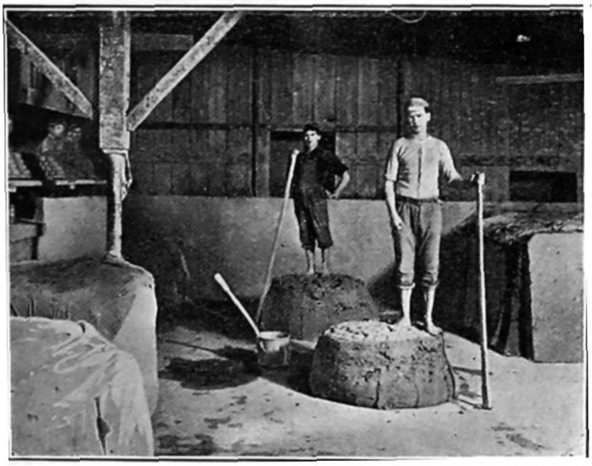
[1] Hot water is usually more effective than cold.

[2] This souring is of very great importance. The longer the time allowed for it the better will be the quality of the pots. Most British makers of glass pots fail to realise how much a souring lasting several months or even years would improve the quality of the goods.

sary. It is by no means unusual for the souring to occupy six months or more. Sometimes the clay is pugged before being trodden or in addition to the treading, but pugging usually produces too soft a paste.[1] It is most important that no water should be added after the first pugging, or the clay will not "age" properly.

Another method consists of mixing the dry materials together, sprinkling them with water, and turning the mixture over with spades. After two days the mixture is passed through a pug mill several times in succession, and is then cut into blocks, which are piled up in a cool place. The mass is compressed by beating it with wooden mallets, and is then allowed to stand for several weeks, after which it is again pugged and stored, these operations being continued until the paste is ready for use. The disadvantage of this method is that irregularity in the mixture is less readily detected than in trodden clay, and, consequently, the proportion of damaged pots may be larger. When so much time and money are spent in making a glass pot, the manufacturers are naturally loth to run risks, and, consequently, prefer to continue to employ "treaders," even though mechanical mixers may be equally effective and cheaper.



(By the courtesy of Mr. C. O. Grafton.)

FIG. 142.—Treading clay for glass pots.

A further objection to pug mills is the introduction of air-bubbles in the clay paste; these fill with water at a later stage and become a source of weakness, or they make the material too porous when in use. Air-bubbles can also be introduced by an inexperienced treader, and such a man should, therefore, work apart from the others until his reliability has been proved. An excellent plan is to finish the mixing of the paste in a wet pan or tempering mill; a still better process consists in passing the material through a de-airing machine (p. 606).

Adequate mixing or blending is essential, particularly when two or more materials are used; otherwise, highly irregular results may be obtained when the pots are in use.

When grog is employed, it should be soaked in water for several hours

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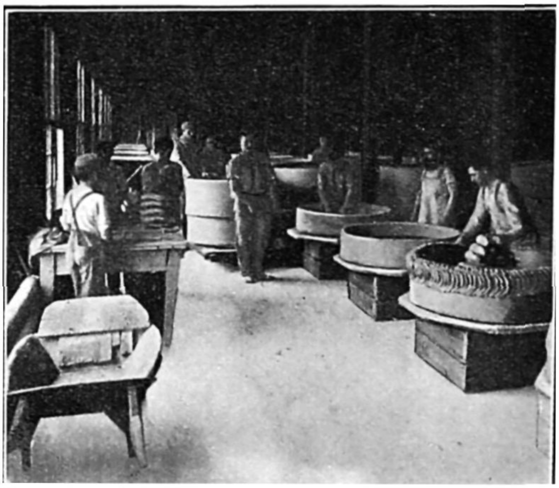
[1] It is interesting to compare this method with that used when making paste for crucibles.

before it is used, or it will withdraw moisture from the clay, and a homogeneous paste with uniformly distributed water cannot be produced.

Where the casting process is used, the clays and water are made up into a slip as described on p. 651. Where several clays are employed, it is sometimes better to make each into a separate slip and then to mix the slips very thoroughly. A little finely ground felspar is sometimes added to the materials used for casting in order to produce a denser pot.

Souring.—The importance of adequate souring (p. 643) can scarcely be overrated, but the very prolonged periods (8 to 9 weeks) formerly considered necessary are probably excessive if the materials have been properly ground, adequately wetted and thoroughly mixed. A period of 24 hours or more appears to be essential to ensure the uniform distribution of water through the paste. Clay-slips are also improved by storage for several days.



(By the courtesy of Mr. C. O. Grafton.)

FIG. 143.—Modelling glass pots.

Making.—Glass pots are chiefly made by hand, with or without a mould; the use of jiggers and mechanical presses is regarded as impracticable, but casting has been used with great success by Weber and others.[1] Making without a mould is termed *modelling*.

When no mould is used, the maker places a circular board, of rather larger diameter than the pot to be made, on a bench or support of convenient height, taking care that the board is quite level, rigid, and steady. The surface of this board is sprinkled with coarse grog so as to form a " bed " about ¼ inch thick, or else the board is soaked in water and covered with a piece of wet sackcloth. To keep the grog together, it is desirable to lay on the board an iron ring, of the same diameter as the bottom of the pot and made in two pieces which can be separated, and to fill the space inside the ring level with coarse grog. When the pot is complete, the ring is removed and the pot can dry regularly with due facility for shrinkage. Some makers prefer to beat out a

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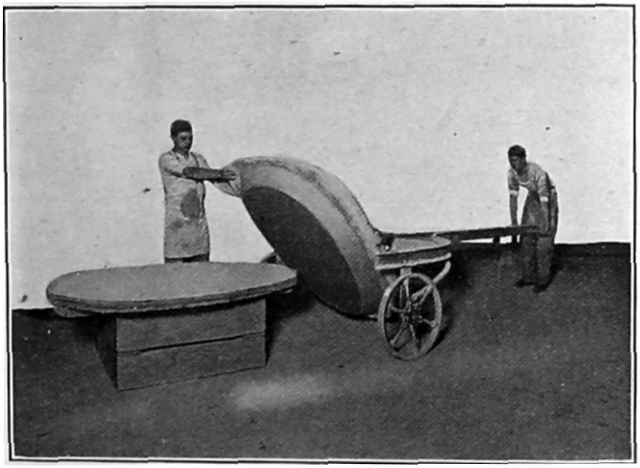
[1] A detailed description of the methods of making glass-house pots used in Germany in 1930 is given in *J. Soc. Glass Tech.*, 1930, **14** (55), 107. For further information on English methods see *ibid.*, 1930, **14**, 119.

circular slab of clay paste about 1 inch thick, scatter a little clay-dust on the surface, and use this as a foundation on which to build the pot. The clay slab shrinks and cracks, but this does not matter, as it prevents the bottom of the pot from doing so. Wet slabs of plaster of Paris or of burned fireclay are sometimes used instead of the foregoing, but only for small pots. It is necessary to allow the paste to creep, as glass pots shrink $1\frac{1}{2}$ to 4 inches during drying.

Having prepared the bottom board, as described, the workman turns to another similar board, mounted on trunnions so that it may be completely inverted when required. On this board, the pot-maker throws with great force small masses of clay paste, each about 8 inches by 4 inches by 3 inches, which he cuts from the main mass by means of a wire or spade. Sufficient of these pieces must be used to form the bottom of the pot, and each piece must be thrown in such a manner that no air is imprisoned beneath it. It is desirable to make the bottom in four layers, each at an angle to the others, so that the effect of any irregularity in the clay may be neutralised by the layer above it. The mass of clay paste thus produced will be about 5 inches thick; it is beaten and worked[1] until it forms a slab of uniform texture and thickness with a smooth surface. The board and slab are then inverted (fig. 144), so that the slab of paste lies uniformly on the bottom board, previously prepared to receive it, and on which the pot is to be made.[2]



(By the courtesy of Mr. C. O. Grafton.)

FIG. 144.—Turning the bottom of a glass pot.

As the outer portion of the bottom of the pot is less solid than the remainder, some makers cut off a strip about 2 inches wide from the circumference.

To form the sides of the pot, the edges of the slab are pressed down slightly with the hand, and, on the depressed portion, a ring of paste is built up in the same manner as the slab was formed, but using much smaller pieces of paste;

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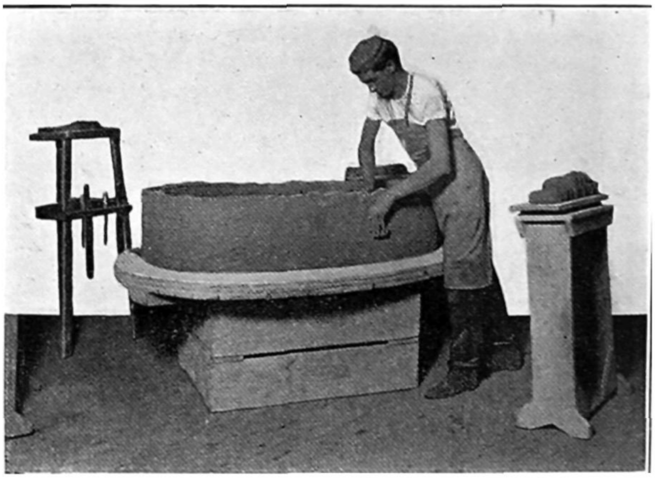
[1] It is necessary to spare no pains in making the bottom as uniform as possible. To secure this, many pot-makers prefer to build up the mass of paste by using much smaller pieces, scraping off portions with the fingers and pressing heavily with the ball of the thumb on to the paste. This process is repeated indefinitely over each part of the bottom until the latter is complete.

[2] Some makers do not trouble to invert the base, but make the bottom of the pot on the prepared board.

this ring forms the lower part of the sides of the pot. To keep the sides upright, the maker holds one hand against the clay and presses the clay with his other hand, working alternately in opposite directions both inside and outside the pot (figs. 145, 146). The "ring" is smoothed both inside and out, the top is roughened with a metal comb, and then the height of the ring is increased by throwing on to it a further series of lumps of paste and working these into a uniform mass with the lower ring. The sides of the pot are gradually built up in this way until they are about 9 inches high. The workman then covers the paste with a cloth and moves to another pot, leaving



(By the courtesy of Mr. C. O. Grafton.)

FIG. 145.—Working finger courses and filling in.

(By the courtesy of Mr. C. O. Grafton.)

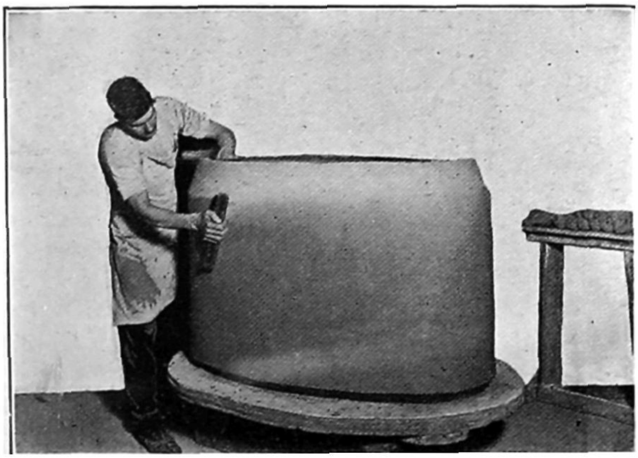
FIG. 146.—Putting on hand courses.

the first one for about twenty-four hours, in order that the paste may stiffen slightly and so be able to bear the weight of further material without squatting.

The height of the sides is then increased by a further amount, depending on the stiffness of the paste and the height of the pot, plenty of time being allowed for stiffening. After the first day it is not usual to increase the height by more than 2 or 3 inches each day, except in the case of small pots, when an increase of 6 inches may be made.

This process is continued, with suitable pauses for the paste to stiffen, until the pot is sufficiently tall or until the springer of the crown is reached. An open pot (fig. 137) must then be finished by carefully scraping or rubbing off any irregularities in the surface. This will not take long if the maker is skilled at his work and finishes each day's work before he leaves it.

If a covered pot (fig. 139) is being made, the bottom and sides are made as described for an open pot, but the top is always built up by hand by adding material to the sides and turning it slightly inward, so as to form the crown or cover (fig. 147). As this crown is comparatively thin and has only to bear its own weight, it can usually be completed within three days. The centre of the crown is usually made separately and is added last; it is dropped into position and then tapped gently so as to seal it (fig. 148). The air inside the pot is sufficiently compressed to support the crown. Some makers cut a hole where the hood will be fixed later, and then insert one hand through this opening, using this hand to "finish" the inside of the crown. In any case, a small opening must be made soon after the crown is completed or the pot will crack.



(By the courtesy of Mr. C. O. Grafton.)

FIG. 147.—Turning the shoulder and starting the crown of the pot.

The top should be thin—the thinner the better—as its sole purpose is to act as a cover. A thickness of 1 inch is ample, even with the largest pots, and a thinner cap is often preferable.

The mouth and hood are made by attaching clay paste around the opening and then modelling it to the desired shape. It is advisable, when making such pots, to form the lower part (or "pad") of the hood so that it[1] will be

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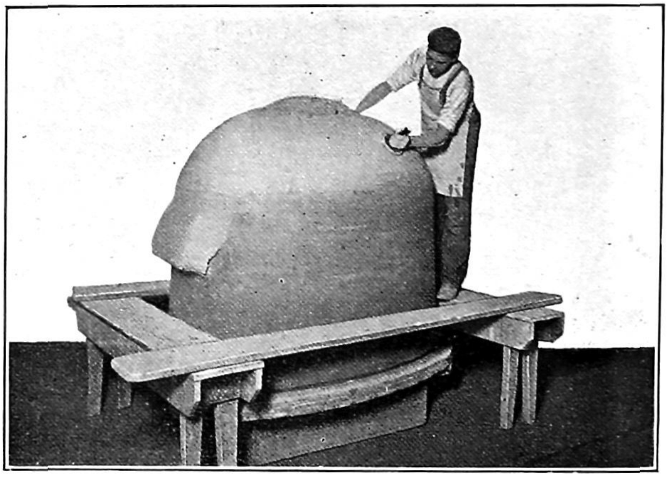
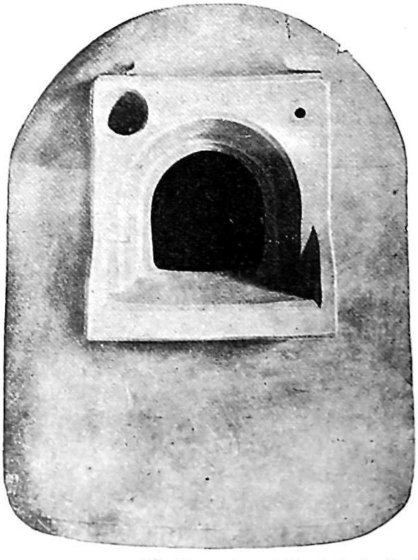
[1] This pad is shown as a projection at the left-hand side of the pot in fig. 148. The whole hood and mouth are shown clearly in fig. 149.

stiff enough to support the remainder of the hood. When the hood and mouth have been completed, the surface of the pot is smoothed and finished. About four months are usually needed to model a large pot.



(*By the courtesy of Mr. C. O. Grafton.*)

FIG. 148.—Finishing the crown of a glass pot.



(*By the courtesy of Mr. C. O. Grafton.*)

FIG. 149.—The finished glass pot.

When partitions, scum-retainers, and other fittings inside the pot are required, they are added during the building of the pot. To make good pots by hand requires considerable skill, and only conscientious men should be employed for this purpose. Only a very small proportion of the boys who start to make glass pots ever succeed in becoming skilled workmen.

Pots made by hand in the manner just described are not so smooth and accurate in form as those made with a mould, but they usually prove more durable, as the process of building causes air-bubbles to be removed from the clay, there are fewer strains in the material, and less liability to crack.

German manufacturers consider that a daily beating of the paste, to consolidate it, is essential to the production of a durable pot, and this beating cannot be done without a mould. With equally careful and skilled workmen, however, there is little to choose between hand-made pots and those in which a mould is used. Broadly speaking, British and American glass pots are built up as described on p. 644, whereas German, Belgian, and French glass pots are usually moulded or cast.

C. W. Thomas has suggested that the inside surface of the pot could be better finished, and so rendered stronger and more resistant to the attack of the molten glass, by making the pot and crown separately and fitting them together with a grooved joint containing a piece of asbestos which is cemented in so as to make a perfectly gas-tight joint. The crown should be made at the same time as the pot, should be placed on the latter as soon as possible, and both should be dried together so as to ensure proper fitting.

Moulding glass pots requires less skill than building them up as described above. The mould consists of several loose pieces of wood which are held together by two iron bands so as to form a kind of tub (fig. 150). This mould is placed on and fastened by clamps or bolts to a level board, the surface of which is covered with coarse grog to a depth of ½ inch to 1 inch. The inside of the mould is covered with vertical strips of wet calico to prevent the clay paste adhering too closely to the wood. The bottom of the pot is formed in the same manner as described on p. 645;[1] the sides of the mould are then attached and the sides of the pot are made by throwing lumps of paste into the mould against the wood, commencing at the bottom and gradually rising towards the top. The thickness is regulated by the maker, who scrapes off the superfluous clay with his fingers and with a small metal comb or scraper. Special care is needed to make an effective union between the bottom and the lower part of the sides of the pot, and this is where unskilled men usually fail. The paste is compressed and consolidated by beating it with a wooden tool or by kneading it with the fingers during the process of shaping the pot. The top of the pot is rounded, as a sharp edge chips readily, and the inner surface of the pot is then smoothed by rubbing with a pad of leather, rubber, or linoleum, so as to make it compact and to form a "skin" which will resist the action of fluxes, etc., as much as possible.

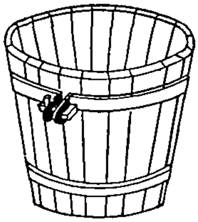


FIG. 150.—Glass pot mould.

Each day the interior surface of the pot is beaten with a polished tool so as to increase its density, compactness, and resistance to corrosion. When the paste is sufficiently dry for further beating to damage its surface, the treatment is stopped. This beating should be regulated so that all parts of the pot are made equally hard. Thus, the top—which dries first—requires to be beaten for a shorter time than the lower part of the pot, which dries last.

The accuracy of the shape of the pot in the mould may be ascertained by measurement, but it is simpler to use a profile (fig. 151), consisting of laths

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[1] Some makers stand inside the mould and form the bottom by working the paste with their naked feet.

forming a structure of the same shape as a section of the inside of the pot. On placing this profile in the pot and turning it round, any irregularities in shape will be detected.

It is necessary to make the inside of glass pots very smooth, as rough portions are more readily attacked by the glass-forming materials.

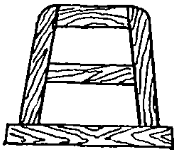
FIG. 151.—Pot profile.

About a fortnight after the making has been completed, the iron bands are released and the mould—which then falls to pieces—is removed. The outside of the pot is rubbed smooth, the rim is rounded, and a knife is run around the bottom of the pot to chamfer it and facilitate lifting it when in use; the serial number is then marked on by means of a nail or metal stamp. A cover of wet cloths is placed on the pot, which is allowed to mature and then dry.

A better method of using this kind of mould consists in throwing into it clay paste sufficient to make a pot, then consolidating it by treading[1] with naked feet or by repeated rammings, gradually working a hollow in the paste, and forcing it higher up the sides of the mould. In this way, the paste is given the desired shape of the pot, after which it is smoothed and set aside to dry. This method, though slower than the one in which the paste is thrown directly on to the sides of the mould, gives a better pot, as it avoids the "joints" which form a source of weakness and cannot be entirely prevented when the latter method is used. Moreover, when the paste is thrown on to the sides of the mould, the pot is less uniform in texture and so is less durable than when it is made from the solid mass. The paste may be further consolidated by beating it daily, as described on p. 649.

Another form of mould consists of a wooden core (fig. 152) and an outer part made in two pieces. The latter are fastened together and bolted on to the same base as the core.

The clay paste is pushed, in small pieces at a time, between the core and the outer mould and is rammed tightly with an iron tool, the lower end of which is roughened. This tool must not be too light; it should weigh at least 7 lbs. It is necessary to ram each piece tightly and to work in a systematic manner so as to obtain a pot of uniform texture. When the mould is filled, the paste is scraped off level, rubbed smooth with a sponge and water, and straw is then laid on the mould. A board is laid on the top and the mould with its contents is inverted quickly. The bolts are loosened, the mould and core are removed, and the sides of the pot are made smooth and compact by rubbing. The removal of the outer mould seldom presents any difficulty. The core is often troublesome, making it necessary to use a chain and pulleys

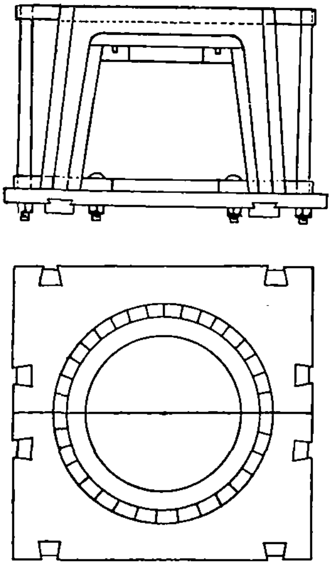
FIG. 152.—Glass pot mould.

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[1] Some makers stand inside the mould and form the bottom by working the paste with their naked feet.

and to twist the core to the right and left alternately whilst lifting it. If the bottom of the core is made loose, so that the sides are lifted out first, the removal of the core is greatly facilitated. It is also wise to remove the core before taking away the outer mould. If the mould and core are well greased with thick oil before use, this will also facilitate their removal. Instead of using oil, some men line the mould and cover the core with sheet zinc. If a paste of suitable stiffness is used and the mould is properly filled, this method produces pots of excellent quality.

None of the foregoing methods of moulding is satisfactory for covered pots (fig. 139), as the compressed paste in the mould seldom unites well with the more open paste used for modelling the cover. To support the cover during its construction and drying, G. M. Bowen (Eng. Pat. 106,871) has suggested the insertion of an inflatable support or balloon which can be deflated when it is no longer required. It is necessary to permit some of the air to escape during the contraction of the pot in drying.

Casting has been found by Weber[1] and others to be an excellent method for making glass pots, but it requires to be carried out with a specially prepared slip on account of the thickness of the walls of the pots. The plant used in this method of casting glass pots consists of a conveyor and mixer or pug mill in which the dry clay and grog, previously crushed[2] and weighed out in the correct proportions and with the addition of a suitable quantity of water, are converted into a uniform paste which is fed in a steady stream to a blunger. Simultaneously, a stream of water, containing the baryta, caustic soda, or other liquefying substance, is run into the blunger. The rotary blades in the latter rapidly effect the formation of a fluid slip and raise the mixture to the desired temperature. Meanwhile, the mould to be filled is placed on a wagon immediately below the outlet of the blunger, and, as soon as the slip is ready, it is run into the mould. The latter is moved out of the way and allowed to stand until a sufficiently thick deposit has been formed in the interior of the mould, after which any superfluous fluid is run off and the core removed. After a further twenty-four hours, the outer part of the mould is removed and the surfaces of the glass pot dressed. The pot then requires to be dried carefully.

In order to cast a mixture rich in grog, the proportion of water present must be small—under 30 per cent.—and the viscosity of the mixture must be reduced by the addition of about 0·1 per cent. of a suitable substance such as alkali or baryta. The slip should be made in the correct manner, *i.e.* the required amount of salts should first be mixed with the amount of water required for the whole of the materials, and, when the salts are dissolved, the clays should be added and made into a slip. Not until this slip is uniform should the grog, felspar, flint, and any other non-plastic ingredients be added, as if all the ingredients are added at once an unduly large proportion of water will be needed, and this causes difficulties. Care should be taken that the variations in the moisture-content of the materials are allowed for, as it is important to keep the composition accurate within very narrow limits. If scraps of waste clay are used, they should be dried thoroughly first, as moist scrap introduces serious variations into the moisture-content of the slip.

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[1] For the proportions of ingredients used in Weber's process see p. 612. In the manufacture of porcelain glass-house pots, as recommended for optical glass by J. W. Wright and D. H. Fuller, about 0·01 per cent. of barium carbonate (to remove any soluble sulphates) and 0·20 to 0·33 per cent. each of sodium carbonate and silicate should be added. The specific gravity of the casting slip should be between 1·90 and 1·95. Such a slip will form a solid casting which may be removed in about seventeen hours.

[2] Casting slips may be made with grog particles up to 0·4 inch diameter.

The mixing must be thorough and not a mere stirring by hand; it may be effected satisfactorily in a blunger.

It is also important to use the slip at a suitable temperature (which depends on the clays used), and to keep it in motion with a mechanical stirrer until the slip has flowed into the mould. Increasing the temperature of the slip has the same effect as adding more salts, but a decrease in temperature reduces the effect of the salts present.

The moulds should be made of plaster of Paris, as they are required to be absorbent. They consist of a base, shell or case, ring, and core, the shell and ring being well bound with steel bands and the core tapering sufficiently to allow lifting through the ring. A funnel with three openings passing through the ring into the mould delivers the slip. All metallic parts through which the slip flows should be made of galvanised iron. A vacuum mould has several advantages over the plain type. A more complicated method consists in using an internal and external mould patented by B. J. Allen, both being connected by pipes to a vacuum chamber. The two moulds when fitted together are such that the distance between them gives the exact thickness of the pot, so that the slip may be poured through a long funnel into the space between them until it is quite full, and then allowed to stand a short time until the clay is sufficiently dry to be removed from the mould with safety. In this way, it is possible to obtain perfectly homogeneous articles having a smooth surface both on the interior and exterior of the pot, whereas the use of a single mould produces a pot with a slightly rough interior. There is also much less danger of forming a pot with either a hard skin or a soft core. J. H. Partridge[1] claims that a very satisfactory method of making open glass-house pots is to pour a viscous slip (containing 0·2 to 0·5 per cent. of electrolyte) into a mould and then cause a core to descend very slowly into the mould by means of an electrically driven screw. The core is removed after 6 hours by reversing the screw. About 4 minutes are required to insert or withdraw the core.

The life of the moulds depends largely on how they are used, as those which are made specially porous for quick working are not so durable as those of denser plaster, which take longer to dry. Under normal conditions, a well-made mould should produce 200 to 300 pots before it is worn out. After fifty pieces have been made, the inside should be scraped so as to remove any salty deposit on it, and, after removing each piece, the mould should be wiped with a cloth, as by continual absorption and on repeated drying, the moulds become saturated with soluble salts removed from the slips. Such salts accumulate on the surface, and may counteract the normal action of the soda in the slip and so cause difficulties in casting. Excessively dry moulds are not satisfactory.

The pots should usually remain in the moulds for twenty-four to forty-eight hours, after which they must be dried carefully. If the walls of the pot are very thin and the temperature of the room is kept fairly high, the time required before the pot is removed from the mould may be considerably reduced. In some cases, it may be possible to fill the mould late in the afternoon and empty it the following morning. In such cases, the same moulds may be used six days in the week, leaving Sunday for drying them. To facilitate this daily use, the walls of the moulds should be as thin as practicable, and the temperature of the casting-room should be kept at 60° F. to 70° F. by day and 70° F. to 80° F. at night, with good circulation of air. The strength of a thin mould may be increased by using bands or other outside supports, or by reinforcements in the mould, though this latter is less desirable.

The principal difficulties encountered in casting glass-house pots are due

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[1] *J. Soc. Glass Tech.*, 1939, **23**, 149.

to improper preparation of the casting slip and defective manipulation in casting. It is most important that the materials selected should be suitable; thus, ball clay should be avoided and the proportion of plastic clay should be kept low. The proportion of grog should be high, and a little calcined china clay may sometimes be used with advantage. The proportions of the various materials should be carefully adjusted, as the results depend partly on the nature of the clays, etc., used. The electrolytes added should be sufficiently pure or they may cause dark stains on the pots. The slip should also be of the correct consistency for casting, or troubles may arise. This must be ascertained by trial, and is best checked by determining the specific gravity or " weight per pint " of the slip.

Discoloration and staining are sometimes caused by using too thick a slip, or by not pouring it uniformly into the mould, *e.g.* when the slip is poured into the mould in such a manner that it strikes the plaster and then splashes off again. It has been suggested that the defect may be avoided by painting the mould with the slip before pouring in the main portion, but such a method is not really satisfactory.

Grey spots or patches on the thin edges of articles after firing are sometimes due to soda being concentrated in such places on drying.

Iron rust may obtain access to the slip from the blungers or other vessels into which it may be placed, so that special care is needed to avoid it. The use of materials which have been too finely ground sometimes has a similar effect. It has also been suggested that discoloration is produced by the presence of hard places in the mould, which cause the uneven absorption of the water in the slip. There is no means of avoiding this defect except by taking care in the preparation of the plaster for the mould, in keeping the moulds in good condition, and in rejecting them as soon as they become too irregular to use.

The advantages of casting with such a slip, compared with modelling or hand-moulding, are: (*a*) greater uniformity of texture; (*b*) a denser and less permeable body is obtained; (*c*) a larger proportion of grog and, therefore, a smaller one of clay may be used, with consequent increase in the refractoriness of the pot; (*d*) the pots are stronger and less sensitive to sudden changes in temperature than those made by hand, and are, therefore, more durable as well as easier and cheaper to produce; (*e*) skilled labour is not required, as the mould is merely filled, allowed to stand, and then emptied; (*f*) the rate of manufacture is greatly increased, as a pot of the largest size can be made with an hour's labour; (*g*) the cost of manufacture is greatly reduced; and (*h*) the tensile strength of the cast pots is considerably greater than those produced by pressing or other processes. Complaints have been made that cast pots cannot be used at temperatures over 1385° C., whilst hand-made pots may be used up to 1600° C.; on investigation it will usually be found that the fault lies in the composition of the mixture used for the pots, and is not due to the unsuitability of casting as a method of making glass pots.

When pots are made by the process of modelling or by hand-moulding, much depends on the conscientiousness and skill of the worker. By casting, however, this objection is largely removed, as the casting does not require much skill. For this reason, it is possible that hand-making will gradually be abandoned and that cast pots will be used almost exclusively in the future. The process is extremely simple, but requires adaptation to each mixture, some clays requiring more attention in this respect than others. This process has been in regular and successful use for some years in several important works.

For further information on casting see pp. 611–616.

Moulding by Compressed Air.—Some experiments by the author in 1916, using a "cement gun" and blowing a suitable paste into a mould, appeared to offer considerable promise but were not developed. The process was cheaper than hand-moulding, but much more expensive than slip-casting.

Casting of Fused Material.—The use, for casting, of a fused mixture of alumina and silica, or of aluminium silicate, was patented in 1932 (Eng. Pat. 402,160), but does not appear to have been developed commercially. Difficulties in connection with moulds make the casting of pots of molten material very difficult, but this method is very successfully used for tank blocks (p. 664).

Drying.—When a pot has been made and its surface smoothed, it is covered with wet cloths so as to prevent it drying too rapidly and is then placed in a room which is kept at a temperature of 16° C. to 20° C. (60° F. to 68° F.). On no account must the temperature approach the freezing-point of water; it may be raised to 40° C. or more if the air is kept saturated with moisture until the pots have reached that temperature (see later).

During the drying, the pots should stand on a suitable base and not, as is often the case, on the floor of the making shop. Wooden boards are unsatisfactory, as they do not allow the pots to creep sufficiently during the drying; there is a certain amount of friction between the wood and the clay surfaces, which frequently causes the latter to crack at a late stage in the drying, when all danger is thought to be over. Something can be done by using very wet boards, or by sprinkling a fairly thick layer of sand or powdered grog on them, but these are only makeshifts. The use of a sheet of calico on the board is also of little value. The best base on which to dry glass pots is moderately coarse grog, which is placed on the floor of the shop and kept in position by means of a wooden or iron ring which is considerably larger than the pot to be dried. The ring serves as a container for the loose grog and yet can easily be removed when required. The grog is placed on the floor to a depth of about 2 inches; it is then wetted thoroughly, so as to prevent it causing the pot to dry too rapidly at the bottom. When the pot has been removed, the grog is sifted to remove any dust and is then ready to be used over again. A good alternative base is a well-wetted fireclay slab.

The pots must be kept away from windows and doors, also out of direct sunlight and away from all vibration.

If a pot has been moulded, and sometimes if it has been built up by hand, it is beaten thrice daily during the drying, so as to consolidate the material, give it a dense surface, and reduce its sensitiveness to sudden changes in temperature. This beating is considered essential by Continental manufacturers. British makers do not treat the pots so thoroughly, and it is claimed that with cast pots this treatment is unnecessary.

The heating of the drying chambers requires care. It is best effected by one or more small stoves placed some distance away from the pots, but sub-floor flues heated by steam- and hot-water pipes arranged around the walls are sometimes used.

It is very desirable, in the earlier stages of drying (*i.e.* soon after the mould has been taken away) to keep the air of the drying-room saturated with moisture, yet not overcharged with it. The best method is to use a specially built dryer in which the flow of air, its humidity and temperature are all controlled independently. The saturated atmosphere is gradually replaced by an unsaturated one at a slowly increasing temperature, so that the pots are always dried under the most favourable conditions. When such a dryer is not used, the drying may require several months instead of 3 to 5 weeks or even less.

When the pots are sufficiently dry, some makers turn them upside down or lean them against bundles of straw, so that air may gain access to the bottom and dry it fully. If the pot is too large for this, it may be lifted up a few inches and supported on bricks, etc., in such a manner that a current of air can pass beneath it. It is, however, a mistake to stand it on a fresh slab of plaster or burned fireclay.

During the drying the pots must be carefully watched, as, if one part dries more quickly than another, cracks may be produced. This may be prevented by covering the tops of the pots with wet cloths, so that they may not dry too rapidly. After being kept wet for some weeks, the cloths are allowed to dry, or are removed when all danger of cracking is past.

A prolific cause of cracks in glass pots is due to the furnaces or annealing room being situated too close to the making- and drying-rooms, causing " pockets " of warm dry air, which produce eddies and crack the pots.

Setting.—The dried pots are exceedingly weak and tender; unless they are handled skilfully they will be irretrievably spoiled.

The glass pots must be placed in the kiln with the greatest possible care, all shocks and blows being avoided; they should not be placed too near the fireplaces or outlet flues, and must be kept free from all flames, or the pots will be liable to crack.

The best method of setting is to carry the pot on a kind of stretcher (sometimes termed a hand-barrow), and to lift it gently from this on to a slab whose thickness is sufficient to make it level with the top of the stretcher. If preferred, the pots can be supported on three or more rolls made of stiff clay paste, so that the air and heat may circulate all round them.

Annealing, Tempering, or Baking.—Glass pots are seldom fully burned by the manufacturers, it being customary to *temper* them by heating to about 1000° C. (Seger Cone 05*a*) in a very low kiln or " pot arch " of the Newcastle type to give them ample strength for transport, etc., the remainder of the " burning " being effected in the glass furnace in which the pots are to be used. Coal-fired annealing kilns are often preferred to those fired by gas, as some firemen consider that the risks of sudden changes in temperature are less; a properly managed gas-fired kiln is more uniform than a coal-fired one.

The kiln must be cleaned before use, any adherent material being removed and any defective parts made good with refractory mortar (Chapter XVII.) to prevent draughts which might crack the pots.

A little powdered glass (cullet) is usually rubbed into the hot pots so as to fill any pores or minute holes in the latter.

The heat must be gentle at first,[1] and no currents of cold air must come in contact with the pots. It is usually wise to keep the damper closed for the first six hours, but afterwards it may be opened slightly and then more and more as the heat progresses, so that a bright red heat is obtained in about thirty-six hours. This is often maintained for a week or more before the pot is used.

The temperature reached is only sufficient to bake the pots and make them strong enough for transport in this country, but some American firms finish the firing at Cone 12 (1350° C.). When thus fired, the pots should be raised to about 320° C. in five days, from 320° C. to 540° C. in the next five days, should be maintained for 48 to 60 hours at 1350° C., and cooled in about 10 days.

For several reasons, the quality of the pots should be greatly improved

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[1] In the Jena glass works, the pots are wrapped in straw, which burns away when the kiln is heated, but prevents too rapid a heating at first.

by firing them at the highest practicable temperature. Many attempts to increase the finishing temperature have been made by glass manufacturers, but the results have often been disappointing. On the other hand, working on a commercial scale, M. W. Travers[1] has found that the best pots are produced by preheating at 1000° C. before placing them in the furnace, and then subjecting the empty pots to the full heat of the furnace for at least 24 hours. This treatment ensures vitrification, the pot having a conchoidal fracture, and much of the clay being converted into mullite and opaque glassy material, with free grains of stable forms of silica and little unaltered quartz. On melting glass in the pot, the surface of the latter becomes covered with a porcelain-like layer of mullite—the result of the mineralising action of the alkali and the removal of the excess of silica. This layer is protective, as mullite is insoluble in alkaline fluxes. After a pot has been in use for some time, if left empty it may collapse in a few hours. Such old pots show a mass of needle-like crystals of mullite in a glassy matrix. The whole change effected in such a material by heat is made up of the growth of crystals, mainly of mullite, but sometimes corundum is also present.

Transferring.—It is best if the pots can be taken, whilst in a red-hot state, direct from the kiln to the glass furnace; but this is only possible where the pots are made in a glass works. The transfer must be effected with every possible care to avoid draughts or sudden changes in the temperature of the pot. The furnace must be allowed to cool until it is at the same temperature as the tempering kiln, and the transfer must be effected as quickly as possible. The larger the pot, the more necessary are these precautions.

Glass pots may be made in one district, allowed to cool, and then taken to another district to be used, but, for the largest pots, the safest plan is to have the pot manufactory close to the glass works, as even the baked pots do not always satisfactorily stand the shocks and strains of transport.

It is essential that the pots should be properly fired if they are to be durable. The customary method of partly filling the pot with glass batch before the pot has been properly fired is not satisfactory, and many pots never do reach the temperature required in order that they may attain their maximum durability. Whilst it does seem, at first sight, a waste of time and fuel to heat the empty pot to the highest temperature of the furnace, this is really the most satisfactory method, as it ensures the proper heating of the clay, produces the maximum proportion of sillimanite, and in every way conduces to the longevity of the pot. A detailed comparison of pots which have been burned in this way prior to use with those tempered at a red heat and then brought into use will show the inferiority of the latter.

In most cases, but particularly where the pots are to be used for the manufacture of optical glass, they should be burned at a considerably higher temperature than that at which they will be used. By so doing the contamination of the glass by iron compounds is greatly reduced, as the surface of the pots is rendered less soluble by this treatment, and at the same time the durability of the pots is increased.

When the pots are to be stored, they should always be kept in a warm, dry place, preferably at a temperature of 80° F. to 90° F.

Properties of Glass Pots.—The chief requisites of a glass pot are comprised in the statement that it shall have the maximum durability in actual use. For this, it must (*a*) be sufficiently resistant to sudden changes in temperature; (*b*) be adequately refractory; (*c*) have sufficient mechanical strength for it to be lifted when full of molten glass; (*d*) have a high degree of resistance

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[1] *J. Soc. Chem. Ind.*, 1929, **48**, 106.

to corrosion by glass or by the raw materials used in glass-making; and (*e*) the glass must remain free from vesicles, even after prolonged heating.

Structure.—The ideal structure of glass pots, according to M. W. Travers, consists of a network of mullite crystals, interwoven so as to form a strong and sufficiently dense mass with a minimum of glassy matrix.

Refractoriness.—A refractoriness corresponding to Seger Cones 31 to 32 (1690° C. to 1710° C.) is usually ample, as the temperature of a pot is not likely to exceed 1500° C. Even more important than the simple refractoriness is the refractoriness-under-load at a pressure of 50 lbs. per square inch; this should not be less than 1250° C. to 1300° C. The breakdown of glass-house pots is seldom due to low refractoriness, but to chemical reactions between the glass materials and the pot.

Resistance to Corrosion.—This is, at all times, necessary, but is especially so when soda ash, potassium or sodium nitrates are used as ingredients of the glass mixture. W. E. S. Turner has pointed out that corrosion may take place at temperatures considerably below the melting-point of the batch materials as a result of the interaction of the ingredients of the mixture. Corrosiveness depends on two things, according to this authority: (*a*) the melting-point of the source of alkali, and (*b*) the temperature at which it is readily decomposed. Soda ash is more readily decomposed than salt-cake, and gives an alkaline batch which has a more corrosive effect. Chilean saltpetre and potassium and sodium nitrates decompose more readily than soda ash, so that their attack on the pots is very severe. Salt-cake is not naturally so corrosive as is often supposed, but owes its action to the fact that it frequently rises to the surface and there forms a layer of fluid which, being very concentrated, is very corrosive in its action. The raw materials from which glass is made may contain large amounts of lime, lead, and other metallic oxides, and, as explained in Chapters I. and II., these exert a highly corrosive action on fireclay at a high temperature. Barium oxide is very injurious to glass pots, as it rapidly attacks them and dissolves some of the clay and grog. There is no remedy other than making the interior of the pot as smooth as possible. The alkali "flume" of dust from the molten glass may attack the upper part of the pot and cause corrosion.

According to Budnikoff and his collaborators [1] corrosion is greatly reduced if 1·5 to 2·5 per cent. of alumina is present in the glass-batch. The alumina is preferably introduced in the form of felspar or china clay, but other alumina compounds may be used, if sufficiently finely ground.

Glass-house pots made of a mixture of calcined bauxite and fireclay in the proportions necessary to form mullite (see "Mullite Bricks," p. 386) are much more durable than those of fireclay and grog, if a sufficient proportion of mullite has been produced by keeping the pot at or near a temperature of 1400° C. for some hours before it is used.

Sillimanite (calcined cyanite) bonded with clay is also highly resistant to corrosion by glass, but such pots are very difficult to make, as the sillimanite is wholly devoid of plasticity.

Cast fused alumina would be an excellent material, but it has not yet been found possible to cast glass-house pots from molten alumina. If the fused alumina is allowed to cool and is then ground and used as grog much of its resistance to corrosion is lost.

In some cases, as in the manufacture of optical glass, it is very important that the glass should be contaminated as little as possible by materials dissolved from the sides of the pot. For this reason, pots employed for optical glass

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[1] *Glastech. Ber.*, 1931, **9**, (3), 148.

can only be used once. The corrosion of the pot by the glass can never be entirely avoided, but it can be reduced by making the glass pots of a highly refractory material, with as compact and smooth an inner surface as possible. Porous pots and those made of very coarse grog are more rapidly destroyed by "drilling" or corrosion than those whose interior is covered with a smooth, dense "skin," as the glass penetrates the pores, fusing the clay and loosening large pieces from the pot, which then cause "stones" or "seeds" in the molten glass. When sufficient matter has been removed in this way, the pot leaks or collapses. Glass pots should also wear smoothly, and must, therefore, be made of particles of medium or small sizes.

The resistance to fluxes and corrosion depends far more on the physical texture of the pots than on their chemical composition.

Mechanical Strength.—The weight and pressure of the glass in a pot are often very great, and it is, therefore, necessary that the pots should have great mechanical strength when heated. In making plate glass, the pots, full of molten glass, are lifted out of the furnace and taken to the casting bed; hence, specially strong pots are required for this purpose. Bulging sometimes occurs in glass pots on account of the great pressure of the molten glass. This is a sign that the pots are either too thin or not sufficiently refractory, and either thicker pots or those made of more suitable materials should be substituted. In many cases, however, the failure of glass pots is due to carelessness on the part of the workmen rather than to any inherent defect in the pots, as in the case of a fireman who, neglecting his work and then suddenly wanting a hotter fire, stokes up rapidly and oversteps the limiting temperature, making the pot soft and, therefore, weak. In bad cases, several pots fail simultaneously. It is preferable to employ an electric pyrometer to record the temperature variations of the pots, or if this instrument be considered too delicate, a few Seger cones, placed near the pots in the furnace, will soon indicate whether the heat has been excessive; these cones do not, however, record the changes in temperature, but only the maximum temperature reached. It is also helpful to put a little more "batch" into the pots which break most readily, so that they cannot heat up quite so quickly and are, therefore, less liable to become overheated. There is little or no danger of overheating so long as the pots contain any unfused glass, as the temperature of the mix cannot rise excessively until the whole of it is in a molten condition, but immediately the mass is fused any additional heat goes towards raising its temperature, and unless great care is taken the pot may be spoiled.

The best test for ascertaining whether a pot-material is likely to have sufficient mechanical strength when in use is to determine the *refractoriness-under-load* (p. 356). Under a pressure of 28 lbs. per square inch a test-piece 2 inches high and 2 inches diameter should not be reduced in height more than 5 per cent. at any temperature below 1400° C.

The crushing strength when cold is much less valuable as an indication of strength; it should not be less than 1 ton per square inch.

Empty pots, when kept in the furnace, lose their shape more rapidly than those containing unmelted batch. For this reason, it is useless to stand empty pots in the furnace in order to test their power of heat resistance.

The *thermal conductivity* of glass-house pots is very important, as the satisfactory melting of the glass and the economic working of the furnace depend almost entirely on this property. As the pots must necessarily be made of material of low thermal conductivity (carbon pots being regarded, at present, as impracticable), the best means of ensuring the maximum thermal conductivity is to use thin pots, but, unfortunately, such pots are not so strong as might be desired.

There are possibilities of some other refractory materials, such as zirconia, being used in glass manufacture to replace the clay pots, though as yet little has been accomplished with them.

Porosity.—The porosity (water absorption) of hand-made pots is usually 20 to 28 per cent., that of cast pots 18 to 23 per cent. No great reduction in the porosity appears to be practicable, as dense pots are too sensitive to sudden changes in temperature and would crack the first time they were used.

Shrinkage in use may be a source of weakness. Pots made of a siliceous mixture shrink less than those made wholly of clay. Most pots tend to shrink most at the lower part of the interior.

Effect of Changing Temperature.—It is of great importance that glass pots should not be sensitive to sudden changes in temperature. This insensitiveness is aided by the use of a large proportion of grog.

The grog must not be too fine or it will increase the spalling. It is worth while experimenting so as to ascertain the best sizes of grog particles and the best proportion of each for pots in each works.

Durability.—The precise length of time which a glass pot can remain in use varies with the kind of glass made in it. If the necessary skill and care are used, covered glass pots may be expected to last for a year or more. Open pots, especially if they are frequently lifted out of the furnace, will be far less durable. Pots for making the best optical glass can only be used once.

The durability of glass pots depends on (*a*) suitable materials, (*b*) effective mixing, (*c*) skilled making, (*d*) the size and shape of the pots and the relative thickness of the various parts, (*e*) the kind of glass to be made, (*f*) the temperature reached, and (*g*) any special conditions which may exist and tend to affect the durability. These have all been dealt with in the present chapter, but it is important to note that many of the properties required in a glass pot are mutually incompatible and a compromise is necessary. Thus, resistance to sudden changes in temperature is best obtained by the use of a porous material, but resistance to corrosion requires a material with a dense and impervious surface and, preferably, a dense and impervious texture throughout. It is, therefore, necessary to exercise the greatest care in preparing glass pots, or unsatisfactory ones may be produced.

The durability of glass pots may be greatly increased by heating them gradually to the full working temperature and maintaining them at that temperature for some hours prior to using them. Travers has shown that by this treatment a larger percentage of crystalline sillimanite is formed than when the pots are treated in the ordinary manner.

The resistance of the pots to flames and their durability may also be increased if they are coated externally with a thin wash of carborundum. A similar wash may be applied to the inside of the pots, though this has the disadvantage of discolouring the glass (see Glazing).

Glazing the outside of glass pots has been tried as a means of reducing their permeability to gases, but has not been successful, because it has too serious an effect on the refractoriness of the pots. It has, however, been found desirable, in some cases, to glaze the interior of glass pots used for very corrosive lead glasses so as to reduce their effect on the pot.

Fixed linings, or internal coatings other than glaze, have been suggested, but have not proved very satisfactory, though in some works they appear to be beneficial. Thus, S. R. Scholes suggested a lining consisting of 90 parts of pot batch and 10 parts of felspar, which was placed in the interior of the pot to a short distance above the highest level likely to be reached by the molten glass. The lining is inserted whilst the pot is being made, and when in use it develops a very dense structure, and enables excellent glass to be prepared with very little risk of the formation of stones. Some users of pots lined in this way claim that they last two or three times as long as unlined ones. The principal difficulty is that the lining and pot do not shrink uniformly, with the result that the lining cracks, so that some glass penetrates behind the lining and causes some of the latter to break off and spoil the glass; this defect is not serious if reasonable care is taken.

A type of lining which appears to have little to recommend it is one patented by C. F. Curtis, consisting of sawdust 30 parts, Portland cement 30, whiting 10, and waste residue from pyrites furnaces 30 parts. A much more useful suggestion, though one not free from objections, is that of W. Rosenhain, who recommended the employment of a ring of zirconia at the level of the surface of the molten glass, because at this point the corrosive action of the melt is most active and serious, whilst zirconia, being very little attacked by the molten materials, would prevent excessive corrosion.

The formation of a lining—by introducing a finely ground substance of a refractory nature into an air or oxygen blast, with or without coal-gas—was patented in 1932 (Eng. Pat. 402,203).

The use of a loose lining made of the same materials as the pot, but of different grain-size, has been suggested, but has not been largely used.

A lining made of calcined cyanite (" sillimanite ") or similar material, bonded with clay, was suggested by Efremov and Kumanin in 1934.

Removable linings have been tried but have not become popular, as some glass manufacturers complain that although they wear well and prevent overheating, they produce a rather pasty melt which results in glass of poor quality.

Provided glass pots are made of a good refractory clay or clays, together with a suitable grog, the materials being properly graded, thoroughly mixed, well made, and skilfully fired, there need be little anxiety on the part of the makers as to the pots being satisfactory. Any defects will then be due to improper use, and principally to overheating.

Defects in Glass Pots.—The chief preventative of defects is the most thorough and painstaking care on the part of the men employed. Among the chief sources of defects are impurities in the clay or grog, improper proportions, incorrect sizes of particles, too much water, insufficient mixing and souring, and carelessness in making, drying, or annealing. Many pots are made defective by improper or careless use.

The principal defects likely to occur in glass pots are—

(i) *Pitting*, caused by an insufficiently burned and too porous body. In extreme cases, the pitting is so deep that holes are formed right through the pot. These may be due to the nature of the contents, but they are often caused by the presence of iron in some form, such as pyrites, in which it is easily attacked. It is known that a glass pot containing pyrites has been pierced through in three hours. If the iron compound is sufficiently finely ground beforehand and is well disseminated through the mass, this substance does not seriously harm the pots.

(ii) *External cracking*, caused by sudden changes in the temperature of the pot, is due to irregular firing or to the admission of cold air. When gas-fired furnaces are used, external cracks in the pots seldom occur, though they tend to the formation of vertical cracks inside the pot, probably caused by the cooling effect of the cold materials put into the pot, as thinner pots do not suffer from this disadvantage. Some glass pots crack at the bottom on account of that part not being heated to a sufficiently high temperature before the pots are filled with the glass-making materials. The remedy is obvious.

(iii) *Internal cracking*, due to: (*a*) insufficient care in drying or in heating the pots; (*b*) not maintaining the pots sufficiently long at the maximum temperature of the pot-arch before moving into the furnace; (*c*) raising the temperature too quickly, especially at 200° C. to 600° C. and at 820° C. to 1250° C.; (*d*) introducing the batch too quickly or into too cool a pot; (*e*) excessive differences in temperature between the outside and the inside of the pot (a difference of 250° C. is common); (*f*) excessive shrinkage of parts of the pots—usually the result of irregular heating, but sometimes due to imperfect mixing of the ingredients; and (*g*) too close a texture, due to the use of too fat a clay or too little grog.

Glass-house pots usually fail without giving any warning, because any tension effect on burned fireclay becomes very serious above 1500° C. They may retain their shape for many hours without any visible sign of expansion, but eventually they fail as the result of the prolonged effect of heat.

(iv) *Distortion* may occur through the glass pots not being sufficiently well supported in the furnace or through irregular heating.

(v) The *excessive solubility* of the sides and bottoms of the pots may cause seeds and similar defects in the glass. This is often regarded as a *corrosion* of the pot by the contents.

(vi) *Corrosion of the exterior of the pot* by dust in the furnace gases.

(vii) *Cracking due to sudden shrinkage* of the pot—usually the result of insufficient heating.

(viii) *Creeping* or gradual flow of the material due to its slight mobility (plasticity) at high temperatures and the outward pressure (simulating the effect of tension) of the molten glass. This is most serious with ball clays, and with mixtures rich in fusible matrix; it is most marked above 1300° C.[1]

(ix) *Black cores*, due to heating the dried pot too rapidly, whereby the surface is partially fused before all the carbonaceous matter has been burnt out.

(x) *Irregular erosion* is usually due to lack of uniformity in texture, or to the use of too coarse a grog or other non-plastic material. There is often a large development of mullite and corundum in the sides (but not the bottom) of the pots, caused by the use of too coarse grog or by irregular heating. The uniform formation of mullite and corundum is desirable, as these are much more resistant than amorphous calcined clay.

(xi) *Discoloration of the glass* is usually due to an excess of iron compounds in the pot, originating in the use of an unsuitable clay or insufficient care in "picking" the clay or grog. For some optical glass kaolin (china clay) is used instead of fireclay, because of the lower iron content.

P. Marson [2] has compiled a long list of defects in glass-house pots, of which the following is a summary:—

Defects due to clay: (i) Too large a proportion of iron compounds or fluxes. (ii) Too large a proportion of carbon. (iii) Contamination during manufacture or transport. (iv) Lack of refractoriness. (v) Grains too coarse. (vi) Plasticity too low. (vii) Shrinkage too high or irregular.

Defects due to grog: (i) Grog is under-burned. (ii) Grog contains black core. (iii) Grog is too coarse or improperly graded. (iv) The composition of the grog is unsuitable.

Defects in the mixture: (i) Inaccurate or careless proportioning. (ii) Due to insufficient mixing. (iii) Due to dirty water. (iv) Due to insufficient soaking or souring. (v) Due to insufficient tempering of the soured paste.

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[1] See also Partridge, *J. Soc. Glass Tech.*, 1939, **23**, 141.

[2] *J. Soc. Glass Tech.*, 1929, **13**, Proc. 12.

Defects in workmanship: (i) Variations in the thickness of the pot. (ii) Inadequate control of the drying. (iii) Vibration during shaping or drying. (iv) Clay paste is too soft or too stiff. (v) Lack of skill or care in shaping, which may also produce a weak laminated structure. (vi) Carelessness in moving the pots.

Many of the defects of glass pots may be avoided by the use of a down-draught instead of an up-draught furnace, as, in the former case, the bottoms of the pots are heated more strongly, the temperature in the furnace as a whole is more uniform, and the tendency to cracking is lessened.

GLASS-HOUSE SUNDRIES.

In addition to bricks and pots, other refractory articles, such as covers, stirrer-sleeves, supports, etc., are required by glass-makers. These are made in wooden or plaster moulds, or are formed by hand from mixtures similar to those used for glass pots. These accessories should be burned at a temperature somewhat higher than they are likely to reach in use, as they should not be porous, nor should they shrink when in use (see Chapters II. and IX.).

The properties required in covers, supports, and other glass-house sundries need no special description, as they are largely the same as those of glass pots.

Rings.—The manufacture of floats or rings for use in melting glass is deserving of more attention than it commonly receives. These rings are placed on the contents of the pot, and facilitate the collection of " scum " and other ingredients which might otherwise become intermixed with the glass when the latter is withdrawn from the pot. These rings should be moderately porous, and should be immersed to at least one-quarter of their depth in the molten glass. They should also be of such a size as not to interfere unduly with the working of the glass beneath them.

The dimensions vary with the size of the pots in which the rings are used, a common size being three-quarters of the inside diameter of the pot, 2½ inches wide, and 2½ inches to 3 inches high. If the glass has a very corrosive action on the rings they may be made rather higher.

The materials of which these floating rings are made are usually the same as those employed for the pots themselves; the clay must occasionally be somewhat leaner, in order that the rings may ride properly on the molten glass. The clays used must be made into an exceptionally uniform paste, as any cracks or fissures in the rings may make them sink. The apparent density of the rings should always be tested; this will show at once whether they are " too heavy " or " too light " for their work. To some extent the weight of a ring will serve as a guide to its suitability, though slight variations in the dimensions of the rings make the use of the weight alone a somewhat rough guide.

Pot-rings made of sillimanite give excellent results. They are expensive in first cost and so are not popular, but as they are very durable they are eventually cheaper, unless broken prematurely.

The rings are usually made in wooden moulds, the material being in the form of a stiff paste of about the consistency of moist soil, which requires to be tamped in order that the mould may be properly filled. The use of as soft a paste as that employed for ordinary clay-working is not desirable; it does not produce a mass of correct density. The burning presents no special difficulty, though the rings should be kept as clean as possible, slag spots and flashes being avoided.

Stirrers should be made of a dense-burning mixture of fireclay and grog, similar in composition to the glass-house pots. They are usually made in wooden or plaster moulds, but may be made very satisfactorily by casting.

GLASS-TANK BLOCKS.

Glass-tank blocks are required to have properties similar to those desired in glass pots, except that, as the blocks are thicker than the walls of the pots, there is less liability of their breaking down under pressure. One of the most important properties required in tank blocks is uniform corrodibility, though this is largely neglected by most manufacturers. In making tank blocks, it is sometimes an advantage to use some siliceous material as grog instead of the usual fireclay grog, as siliceous particles which become detached from the block are more readily dissolved by the glass than fireclay, and so do less harm. For this reason, it is preferable to employ a slightly less resistant material if it will corrode more uniformly than a more refractory one which forms "seeds."

The bricks or blocks used for glass-tank furnaces may be divided into two classes: (i) those used for the sides and bottom of the furnace, and (ii) those used for the roof. In the roof or crown of the furnace there is much less corrosion than in the bottom and sides of the tank, as only volatilised alkalies (" flume ") or occasional splashes of glass can come into contact with the roof. For this reason, it is preferable to employ silica bricks for the construction of the roof, as they tend to expand rather than contract when heated, so there is much less chance of their becoming dislodged, and any particles of silica falling into the bath will do less harm than similar particles of fireclay bricks.

The sides and bottom of the tank require to be equally refractory and also more resistant to corrosion, as they are directly in contact with the glass. It is, therefore, customary for blocks made of fireclay to be employed, though, as previously mentioned, a highly siliceous material may, in some cases, be used with advantage.

The best bricks[1] contain 80 per cent. of alumina and are composed of 40 to 50 per cent. of corundum and mullite, which should be in a crystalline state—the result of proper heat-treatment during the manufacture of the bricks. The texture should be fine and the particles of uniform size and shape.

In recent years, blocks made of other materials have been preferred to those made of fireclay and grog, though the latter are still used in those parts of the furnaces where the corrosion is not excessive. The mixtures of fireclay and grog are usually the same as those used for glass-house pots, but sometimes 2 to 6 per cent. of bentonite is added to make the material easier to work and to facilitate the drying.

In some glass-works in the United States, blocks of natural " fire-stone " are employed in the place of fireclay or silica blocks. Such blocks should have a fine texture, so that they will resist corrosion and will wear away uniformly. At the same time, they must not be so dense as to crack or spall when subjected to sudden changes of temperature, which inevitably occur in working. Blocks with a coarse, open texture should be avoided, as the fine binding clay is easily dissolved and causes particles of block to be disseminated in the glass as " seeds." Some American manufacturers grind the face of the blocks to a dull polish by means of a carborundum wheel applied to the dried but unfired blocks; others grind the fired blocks in a similar manner. This is done to ensure the necessary accuracy of shape and a desirable smoothness of face. Most British glass-makers prefer to leave the natural face untouched, but appreciate the greater durability due to the blocks being ground accurately to size and so being capable of being laid with the thinnest possible joints.

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[1] Fabianic, *J. Amer. Cer. Soc.*, 1935, **18**, 211.

Tank-blocks for glass-melting may be made by any of the following processes:—

(i) Hand-modelling and -moulding.

(ii) Hand-ramming or -tamping.

(iii) Mechanical ramming, using blunt-nosed tools with a pneumatic hammer and applying 300 blows per minute. The best mixture for this process consists of about 80 per cent. of grog or other non-plastic material, 20 per cent. of clay, and 10 per cent. of water.

(iv) Mechanical pressing of a semi-dry or stiff-plastic mixture containing 85 per cent. of grog or other non-plastic material, of which only 1 per cent. remains on a 25-mesh sieve, 15 per cent. of fat clay, and 7 to 10 per cent. of water containing a deflocculant, *e.g.* 0·1 per cent. of sodium silicate. The pressure should be at least 1½ tons per square inch, and up to 5 tons per square inch has been used.

(v) Extrusion (wire-cut process), with or without subsequent pressing.

(vi) Slip-casting (p. 651), using a slip composed of 80 per cent. of grog with sodium carbonate and sodium silicate as deflocculants. Prolonged blunging is essential. A good slip should shrink so that the block can be removed in 24 hours, but it is best to leave it 48 hours before removal. A good slip will weigh 42 oz. per pint and will contain about 17 per cent. of water.

Slip-casting produces blocks with a close texture and requires little skill. This method is being increasingly used on the Continent. In England the use of a vacuum casting process (p. 614) is proving very satisfactory, as it removes the air ordinarily incorporated in the slip during its production and so produces denser and sounder blocks.

(vii) Fusion-casting, which should produce the best blocks, though those made by this process are liable to be spoiled by the presence of "pipes" and "blow-holes" due to faulty casting.

Of these various methods the last gives the best blocks, but they are usually regarded as too costly by those who have not used them for a long period. Of the other methods, slip-casting and ramming have the advantage of enabling blocks to be made with 85 to 90 per cent. of grog (including sillimanite). A vacuum treatment of the mixture, higher and better-controlled firing, and more prolonged soaking have resulted in denser blocks and a reduction of porosity to below 20 per cent.

Sillimanite blocks made of sillimanite (really calcined cyanite, but sold as sillimanite) have given very satisfactory results and are, in many glass-works, found to be much more durable than fireclay blocks (11 months as against 6 weeks). They are made in the same manner as sillimanite bricks (p. 385), but are larger; the precise size depends on the dimensions of the tank.

Turner[1] found that the lowest porosity of sillimanite mixtures is obtained by using 1 part of coarse, 1 part of medium, and 4 parts of fine material. Haller[2] recommends a maximum size of 10-mesh, and prefers 75 per cent. of the grog to lie between 5 and 40 I.M.M. mesh and 15 per cent. less than 80-mesh. In the absence of dry fusion or vitrification, the theoretically densest packing with spheres of uniform size gives 25·9 per cent. porosity. The bond clay should not exceed 26 per cent. if low shrinkage and low porosity are desired. Intense pressure (up to 15 tons per square inch) is necessary to ensure the minimum porosity.

Sillimanite blocks should be burned at 1500° C., otherwise they are too porous and are readily attacked by the glass. When properly made and burned they are remarkably durable.

[1] *J. Soc. Glass Tech.*, 1925, **9**, 334.

[2] *J. Soc. Glass Tech.*, 1931, **15**, 99.

The critical temperature in heating sillimanite blocks is 600° C. to 800° C., and H. Knuth[1] has advocated taking three days to heat them through this range of temperature.

The shrinkage of well-burned sillimanite blocks during use is almost negligible.

Sillimanite blocks should contain at least 32 per cent. of alumina, have a sp. gr. of 3·0 to 3·1, a volume-weight of 2·4 to 2·5, and a porosity not exceeding 20 per cent. by volume. The refractoriness-under-load should be such that no sign of collapse occurs below 1600° C., and no serious loss of shape below 1700° C.

Sillimanite blocks have been used successfully for the superstructure, doghouse, throat, and flux line of glass-melting tank furnaces, tuckstones, charging doors, feeder spouts and feeder parts of all descriptions, and for jets for glass-wool furnaces, burner ports, and cements for hot and cold repairs to tank and pot furnaces.

Mullite blocks are also very satisfactory; they are made in the same manner as mullite bricks (p. 385). The greater the amount of mullite present the more resistant will the blocks be to glass. Transformation to mullite is increased by adding an ochreous clay with a high iron-content,[2] and at 1300° C. to 1380° C. The increased iron-content does not affect the glass, as the corrosion of the pots is much less than usual; according to Budnikoff, two parts of grog and one part of ochre have given very good results.

Corundum blocks are made in the same way as sillimanite and mullite blocks, but have been found by some users to produce less " seeds " in the glass. The use of refractory materials containing 85 to 90 per cent. of alumina was patented in 1936 (U.S. Pat., 2,019,209).

Diaspore blocks, made by fusing diaspore electrically and casting the fused product, are commonly known as Corhart blocks. They are exceptionally durable in glass-melting tanks, but they require special care in casting if unsound blocks are to be avoided. These blocks are expensive in first cost, but owing to their great durability they prove eventually to be cheaper than blocks made of fireclay. Blocks made by casting the fused material have the great advantage of almost negligible porosity. Blocks made wholly of fused diaspore are rapidly disintegrated by molten glass, but by mixing a little kaolin with the diaspore before fusion a stable material is produced.

The use of bricks or blocks made of *wollastonite* ($CaO.SiO_2$) which has been fused and cast was patented in 1930 (Eng. Pat. 371,272).

Silica blocks must usually be made by tamping, preferably with a tool weighing 18 to 22 lbs., with a tamping face 8 inches by 4 inches. The mould is over-filled, so that when the tamping is complete there is a slight surplus to be cut off. Tamping in a series of layers is less satisfactory. The drying requires special care, and during the burning the blocks should be " boxed " so as not to come into direct contact with flames.

All tank-blocks should have a fine texture to resist corrosion and wear.

The best basis of comparison of the durability of different materials used in tank-construction is the number of tons of glass produced per square foot of surface exposed to the glass during the " life " of the part of the tank under consideration. This need not contain the length of life as a factor, as this is indirectly included in the number of tons of glass produced. With fireclay and silica blocks of good quality an average of 20 tons per square foot is usual, but with blocks of fused alumina of the Corhart type figures as high as 87 tons can be reached without difficulty.

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[1] *Glastech. Ber.*, 1936, **13**, 116.

[2] P. Budnikoff, *Ber. deut. ker. Ges.*, 1934, **15**, 505.

As the mortar used in binding the blocks together is usually less resistant to corrosion than the bricks or blocks themselves, it is preferable to have as few joints as possible, and, therefore, blocks are preferable to the standard size of bricks.

Ordinary mortar must never be used when laying tank-blocks. The most suitable material is a slip made by mixing ground fireclay with an equal weight of water. If much residue is left on passing this slip through a 50-mesh sieve, a larger proportion of fireclay should be used and the coarse material separated by sieving.

Selected blocks of silica rock are sometimes employed for lining the upper part of the sides of the furnace, as these do not come into direct contact with the glass. Where such blocks are employed, those used for the sides should be set in the same position as the original bedding of the stone, the ends of the grain pointing into the furnace, whilst the blocks used for the bottom of the furnace should be set perpendicular to the bedding position so as to bring only the ends of the grain into contact with the glass. Shelling or spalling will usually occur if the blocks are placed in any other position. Where artificially prepared blocks are used this precaution is unnecessary. Many tank-blocks made of fireclay are badly burned and consequently contain dark cores. The cause of this defect is described under *Cores* in Chapter II.

Glass-tank blocks may be preserved by cooling them externally by means of a stream of air (alone or saturated with steam) projected from a series of nozzles on to the blocks. This reduces the temperature of the blocks and prevents excessive corrosion, but it is wasteful of heat. In some cases the cost of the loss of heat is less than that of replacing the blocks more frequently. The use of *hollow blocks* was patented in 1936 (U.S. Pat. 2,023,044).

It is important to realise that the problems involved in the manufacture of tank-blocks differ fundamentally in several respects from those in connection with glass-house pots. For this reason, many mixtures, including those containing sillimanite, are eminently suitable for tank-blocks, but are useless for pots.[1] The only book in the English language which deals comprehensively with glass-tank furnaces is a translation by S. R. Scholes of Devillier's *Le Four à Bassin*, published by " The Glass Industry," New York, U.S.A.

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[1] *J. Soc. Glass Tech.*, 1932, **16**, 62, 143.

CHAPTER XIV.

RETORTS.

Retorts are vessels of refractory material which are used for the distillation of coal, zinc, sodium, and other substances. For the distillation of liquids, globular, pear-shaped, or cylindrical retorts are used, but for other purposes retorts usually consist of long tubes of circular, oval, ⌓-shape, or " half-round " cross-section, with one end closed and the other connected to a condenser. The ⌓-shape is preferable where it is possible to employ this form conveniently, as an even layer of coal or other material is obtained which can be heated uniformly without difficulty, whereas difficulties, due to irregular heating, arise in those with curved lower surfaces.

Vertical retorts consist of an upright cylindrical structure, either (i) surrounded by flues up which pass the hot gases for heating the retort, or (ii) through which a current of hot air and steam is passed. These retorts are almost always built of bricks and are, therefore, known as segmental retorts. Some coke-ovens closely resemble vertical retorts in structure, though not in actual use. In all vertical retorts the action of the impurities in the coal on the refractory materials is to produce a slag which gradually destroys the brickwork. This cannot be prevented, but it may be minimised by the use of suitable coal and by careful attention to the texture of the bricks.

Vertical retorts are also damaged by the dislodgment of pieces of the brickwork. This is known as *flaking*, and appears to be due chiefly to the formation of a deposit of closely adhering carbon (*scurf*). When pieces of refractory brick are dislodged without any formation of scurf, the defect is known as *spalling* and is chiefly due to the inability of the refractory material to withstand sudden changes in temperature. Both these defects may be reduced, if not prevented, by using special (non-spalling) bricks in those parts of the retort where the defects chiefly occur. Vertical retorts vary very greatly both in height and width, and no " average " figures can be cited. Equally great variations occur in their design. Vertical retorts are chiefly lined with silica or highly siliceous materials, but all the materials used for horizontal retorts can be employed if desired.

For the distillation of zinc and some other materials, smaller vertical retorts are usually employed, varying from 4 feet to 6 feet in length and 7½ inches to 8½ inches in diameter, with walls 2 inches thick, though much larger ones are preferred in some works.

Segmental retorts (figs. 153, 154) are composed of a series of blocks, bricks, or tiles, preferably tongued and grooved at each end and side. T. W. Keillar has patented the use of hollow blocks of silica or fireclay for segmental retorts, the hollow portion being filled by the insertion of kieselguhr. These segments may be made by hand in moulds like bricks (Chapters II. and III.), or in a machine or press. Great care is required to ensure that the segments are accurate in shape, with good arrises. They should not be subjected to great pressure in manufacture, or they will not resist sudden changes in temperature.

It is surprising that English gas engineers have not adopted segmental retorts more extensively, as, in spite of their slightly higher first cost, experience has proved that they are much more durable than moulded retorts and the leakages are far less. These advantages are due to the greater flexibility of the segmental retorts under changing temperatures and to any cracks which occur falling along the lines of jointing. The latter, being tongued and grooved, render leakage from small cracks almost impossible. The gas-tightness of the segmental retorts depends on the care taken in building and using them; they are more easily damaged by rough treatment in "scurfing." In consequence of this, some engineers have complained that segmental retorts are not satisfactory, but more detailed investigation will usually show that the fault lies with the treatment rather than with the type of retort. The idea that a large number of joints in a retort necessarily increases the leakage is found, in practice, to be erroneous.

Some engineers prefer all the blocks to have grooves, instead of alternate tongues and grooves, as it is difficult to get the blocks so true longitudinally as to ensure an exact fit of the tongue, and faulty joints result. Furthermore, all grooved blocks are reversible, so that a slight curvature in the length can be dealt with, and keying up can, obviously, be more easily and effectively done with such blocks. It is essential that the jointing material for use with these blocks should be carefully chosen. A jointing composed of silica brick, firebrick, silica clay, and fireclay, in equal proportions, finely ground and mixed in a mill, has been found very efficient for the purpose. It is advisable to have the blocks so designed that the transverse joints all occur on the cross-walls. In the case of ⌓-retorts, rectangular shoulder-blocks offer advantages over rounded blocks, being more easily set and adding mechanical strength for machine-operation. The shields can then be constructed of ordinary rectangular silica tiles, in place of special ones.

It is advantageous to construct the upper part of segmental retorts of silica and the base and shoulders of aluminous fireclay, as the latter can better withstand the abrasion of the coke. The ends are more conveniently made by moulding each in one piece about 2 feet long. The mouthpiece should be made of aluminous fireclay, so as the better to resist corrosion by salts.

The cost of large gas retorts could be considerably reduced, or the quality could be improved if certain sizes were recognised as standards. At the present time, many retorts have to be made to order to special patterns; this involves additional cost in labour and necessitates slow delivery.

This standardisation of sizes is one of the reasons why retorts are made more cheaply in Germany than in this country; the workmen there are employed all the year round making for stock, instead of being busy in the early part of the year and slack later. This question of standardisation has been brought forward time after time since 1878, but there has been no definite result up to now. It is very desirable that there should be some agreement among engineers as to the best sections to be adopted as standard ones.

Horizontal segmental retorts vary in size, according to their purpose and use. For the production of illuminating gas from coal, the retorts may be from 6 feet to 20 feet in length, 12 inches to 36 inches wide, and 8 inches to 18 inches high, the walls being usually 3 inches to 4½ inches thick, except at the front or open end, where there is usually a flange to which a door can be bolted. In retorts for chemical purposes, cylindrical or globular shapes are usually preferred.

Retorts are usually arranged in groups of five or more, so as to save space and fuel. They may be placed horizontally, inclined, or vertically, and may be either continuous or intermittent in action.

Retorts may be made either in one piece or in segments; recently, gas engineers have taken a great interest in the use of retorts made in numerous sections, but most other retorts are still made in one piece. The sections may be in the form of short tubes about 18 inches long, or of flat blocks, bricks, or tiles, the sides and ends of which may be so shaped as to key into each other. Retorts which are made in one piece are cheaper in first cost (if the erection is included), but are not so durable as segmental retorts, are less readily repaired, and are more difficult to keep gas-tight.

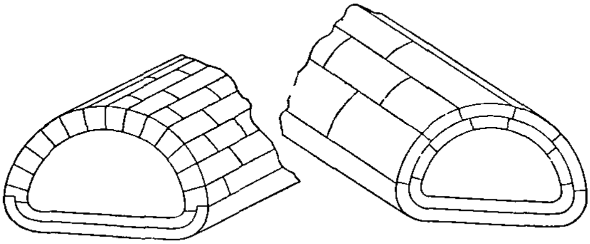


FIG. 153.—Segmental retorts.

The shape and size of retorts must be considered in connection with the materials used in their manufacture, in order that materials of the requisite refractoriness and strength may be obtained. Thus, where a very high temperature is to be attained, a correspondingly refractory material must be employed. Where strength at a high temperature is required, as in the case of vertical retorts, which by virtue of their shape are subject to great pressure, it is necessary to sacrifice some amount of refractoriness in order to secure greater strength.

Materials.—In considering the materials of which retorts can be made, attention should be paid to the varying and largely incongruous conditions which they are called upon to withstand:

(i) They must be highly refractory.

(ii) They must be good heat-conductors and of sufficiently close grain to minimise diffusion.

(iii) They must be capable of resisting wide fluctuations in temperature.

(iv) They must be of sufficient strength and wearing quality for operation by stoking machinery when this is used.

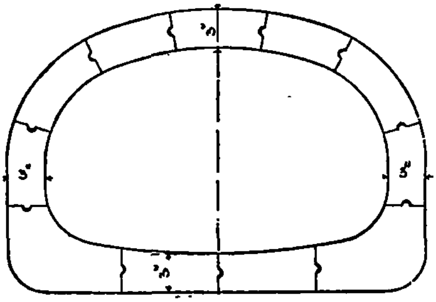
Retorts may be made of (*a*) silica, (*b*) bauxite, (*c*) graphite, (*d*) magnesia, (*e*) silicon carbide, (*f*) chromite, and (*g*) clay. Those made of metal are only suitable for use at relatively low temperatures, and are not described in this volume; retorts made of clay are the most popular, but those made of silica have recently aroused great interest among gas manufacturers.

Silica retorts are increasingly used for coal. In the United States, they are made of a silica rock resembling ganister and containing about 95 per cent. of silica, but the silica retorts used for gas-making in the British Isles are generally made of a mixture of silica and fireclay; some used in Sheffield are made of highly siliceous clays from the East Riding of Yorkshire, and contain about 85 per cent. of silica.

Silica retorts are usually made in tile-like segments (figs. 153, 154), which key into each other so as to produce tight joints. It is desirable that the front 18 inches or so of gas retorts should be made of fireclay, so as to prevent the silica from spalling when the retort is opened and air enters it.

In the manufacture of coal-gas, segmental retorts made of silica, if of good quality, may last twice as long as retorts made of fireclay; they can be used at a higher temperature with less risk of distortion and have a higher thermal conductivity, so that they can deal with a larger quantity of coal. A further minor advantage is that the carbonaceous *scurf* is more easily removed from silica retorts than from those made of fireclay.

The particles of silica are united with a bond—usually lime—the material being treated in exactly the same way as for silica bricks (Chapter III.); with highly siliceous clays, and with some ganister, no bond is necessary, the segments being made as described on p. 667.



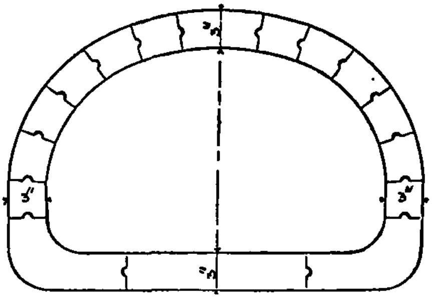


Fig. 154.—Segmental retorts.[1]

Small retorts of fused silica (see Chapter XV.) are made in various sizes; those used commercially have capacities from $\frac{1}{8}$ to $2\frac{3}{4}$ cubic feet. They are specially suitable in the preparation of fine chemicals such as nitric, sulphuric, and hydrochloric acids of special purity, mercuric chloride and bromide, and a large number of the more volatile hydrocarbons. The complete apparatus required for distillation can be made wholly of silica, so that the product does not touch any other material during its manufacture. Such retorts are superior to glass in their higher resistance to acids and in the great rapidity with which they may be heated and cooled. They are also less liable to be broken, as they can be made much thicker than glass retorts.

Retorts built of silica bricks have a higher heat conductivity than those of burned clay, so that silica retorts have a larger coal-carbonising capacity and probably use less fuel than those made of fireclay. Retorts made of silica are understood to be more durable than those made of clay, and more resistant to abrasion.

Silica retorts expand about $\frac{1}{8}$ inch per linear foot when in use,[2] and this

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[1] Figs. 153 and 154 are from the 1914 Report of the Institution of Gas Engineers.

[2] The expansion depends on the physical nature of the silica. The ganister in South Yorkshire has only about half the expansion mentioned in the text.

must be allowed for in designing a retort bench. This slight expansion is often an advantage, as it secures tight joints in segmental retorts, particularly if a piece of cardboard is fitted between each segment.

Silica does not soften so gradually as fireclay, but remains rigid until close to its fusion-point. Hence, a silica retort is stronger under load at working temperatures than is a similar retort made of fireclay. This may, however, prove a serious disadvantage, for if a silica retort is overheated, it will collapse without warning.

Retorts made of silica are not so new as a study of recent literature on the subject suggests. Thus, a retort built in 1902–3 of Dinas bricks has proved quite satisfactory, and for many years the upper portion of the retorts used by the Sheffield Gas Company have been built of local siliceous clays containing 85 per cent. of silica and only 8 per cent. of alumina; more recently, the whole of the settings have been built of this material. These clays have a refractoriness corresponding to Seger Cones 28 to 30.

Silica is superior to fireclay in enabling a larger amount of coal to be carbonised and in having a greater refractoriness-under-load than fireclay, so that it is almost impossible to burn down a setting made of silica, whereas one of fireclay or of semi-silica does occasionally collapse from overheating.

The great drawback to silica as a retort material is its tendency to flake or spall when in use. This may be reduced by sufficient care in manufacture and by burning at a sufficiently high temperature, but it cannot be entirely avoided if lime is used as a bond. By using alum, clay, or a spinel bond and firing at 1500° C. the spalling is still further reduced.

The value of retorts made of silica depends on the care and skill used in their manufacture, and the defects observed by gas engineers who have used inferior or experimental retorts should not be allowed to prejudice the further use of what is undoubtedly a valuable material for gas retorts.

Semi-silica retorts are made of material containing 70 to 84 per cent. of silica. Natural mixtures of clay and silica (see " Pocket Clays," p. 150) may be used, or artificial mixtures of fireclay and ganister, or other form of silica, may be employed. These mixtures have a lower refractoriness than either fireclay or silica, but distortion when under pressure does not occur at so low a temperature as with fireclay. The chief advantage of semi-silica retorts is that they have a slightly higher refractoriness-under-load than those of fireclay. A semi-silica retort should not change in size during the burning.

Bauxite retorts have not been extensively used. F. Leisse has found that retorts made of a mixture of bauxite and fireclay containing between 55 and 60 per cent. of alumina are more durable than those made of clay and grog. The usual reason for adding bauxite, however, is to increase the refractoriness of the fireclay, even at the expense of some mechanical strength.

Graphite retorts are particularly capable of withstanding sudden changes in temperature, and, in this respect, resemble graphite crucibles (Chapter XII.).

The proportion of graphite varies considerably, but a good mixture consists of 2 parts of graphite and 1 part of fireclay. Some mixtures contain too little graphite to justify the name of " graphite retorts." Thus, J. D. Hollingsworth and J. Mitchem have patented the use of a mixture consisting of graphite 14 lbs., fireclay 35 lbs., fireclay cement 59 lbs., and salt 1 lb., the salt being dissolved in the water employed for making the paste. The graphite must be of good quality, and have the characteristics described on p. 191. Graphite retorts are made in the same manner as clay retorts. Hitherto, only the smaller sizes have been made of this material.

Retorts of a different character, and chiefly of value for experimental purposes, were patented by R. P. Pictet in 1913. In their production, finely divided carbon is used; this is prepared by dissociating methane or other hydrocarbon gases. This carbon is mixed with three times its weight of finely powdered silica, alumina, magnesia, lime, carborundum, or other highly refractory material, and is made into a paste with alcohol, chloroform, or water. The retorts are dried and fired at a temperature "sufficient to cause vitrification, but not deformation." As the material of which they are made is electrically conductive, they may be heated by passing an electric current through them (see also "Carbonised Clay").

J. G. Aarts, in 1910, patented the use of carbon with a suitable bond, the mixture being moulded into retorts which are dried and then heated to above 2200° C. in silicon vapour.

Small *magnesia retorts* have been made in Germany from sintered magnesia ground to a fine powder and mixed with one-tenth of its weight of gelatinous silica and sufficient water to form a plastic paste. These retorts have proved useful for heating metals whose oxides have a strongly corrosive action on clay or silica. Such magnesia retorts are made in a similar manner to clay retorts, and, if desired, other bonds, such as those used for magnesia bricks, may be employed.

As magnesia has practically double the heat conductivity of clay, it is advantageous in this respect, but, unfortunately, it is so sensitive to sudden changes in temperature that retorts made of magnesia are only capable of limited use. With a view to overcoming this serious disadvantage, B. Talbot, in 1900, patented a process which consists in soaking the retorts in coal tar, heavy oil, resin, or other liquid hydrocarbon at a temperature of 100° F. The absorbed material is converted into coke when the retort is in use.

Silicon carbide retorts are also known as *carborundum retorts*. Their construction was first patented by A. L. J. Queneau in 1905, fireclay being used as a bond. Such retorts are highly refractory, and are not very sensitive to sudden changes in temperature. They are, however, inferior to fused silica in the latter respect. Retorts made of silicon carbide have, on average, seven times the thermal conductivity of similar retorts made of fireclay or silica.

The initial cost of silicon carbide is very high, but, according to M. Barratt, if the ultimate cost per ton of coal carbonised is taken as the basis of costing, the carbide effects a distinct saving for the following reasons:—

1. Great fuel economy due directly to the high thermal conductivity.
2. Greatly increased effective life, owing to the high refractoriness and to the fact that the flues heating the ovens would not have to carry so excessive a temperature in order to transmit sufficient heat to the interior of the ovens, due to the enormously greater heat-carrying capacity of silicon carbide.
3. A shorter coking period, which would increase the daily output per oven.
4. Freedom from saline corrosion, due to the chemical inactivity of the material.
5. A more uniform transmission of heat, which would result in a more uniform quality of coke.
6. Less loss from abrasion of the charging machinery, owing to the hardness of the material.
7. The strong reducing atmosphere existing in ovens which is so destructive to silica is without action on silicon carbide.
8. The sudden changes of temperature due to charging do not cause either spalling or cracking, owing to the coefficient of expansion being practically nil.

9. The resistance to flying ash and flue-dust is much greater, no slag being formed.

The advantages of this new material for oven walls appear to be so overwhelming as to merit more serious consideration by builders and users of by-product ovens.

G. Simcoe has suggested the addition of 10 to 20 per cent. of carborundum to retorts made of clay.

Carborundum retorts can only be used for zinc ores which are acid in character; for these they are excellent. They may be made of 80 per cent. of carborundum and 20 per cent. of binding clay.

Chromite retorts were patented in 1905 by A. L. J. Queneau, who specified the use of fireclay as a bond.

Clay retorts are made of a mixture of grog and clay. The use of clay alone is unsatisfactory, because it does not produce retorts sufficiently capable of withstanding sudden changes in temperature and should, therefore, be mixed with grog. Clay retorts have been rivalled to some extent by iron ones, but the former are by far preferable for gas-making, as they are capable of producing a greater quantity of gas from a given amount of coal. On the other hand, owing to the increased temperature of the clay retorts, the density of the gas and its illuminating value are less than those of the gas produced in iron retorts. By working clay retorts in such a manner as to produce the same amount of gas as iron retorts, the illuminating power will be the same, but the greater yield of gas of less illuminating power is naturally attractive to gas manufacturers. A further advantage of clay retorts is that the cost of setting them is sometimes 20 per cent. less than for iron retorts. In addition, clay retorts are much more durable and cheaper than iron ones; a good iron retort will seldom last more than one year, whereas a clay retort is expected to last on an average two and a half years. The initial cost of iron retorts is nearly twice that of clay retorts.

Clay retorts are more liable to leak than iron ones, but this can, to some extent, be prevented by proper manipulation of the firing, so that where the coke produced commands a sufficiently high price, the loss through leakage is negligible.

The materials employed for clay retorts are chiefly clay and grog; they should be carefully chosen.

The *grog* may be made of selected fireclay or kaolin,[1] and, for the sake of economy, a moderate proportion of damaged retorts [2] may be ground up and used as grog. These broken retorts must be carefully cleaned before use; those parts which have undergone partial fusion should be rejected.

The grog must be sharply sub-angular, as rounded grains do not form so strong a mass. The particles of grog should be from 0·03 to 0·25 inch in diameter,[3] all finer particles having been removed by screening. Some firms use a little fine grog, but in most cases this is undesirable.

In order to avoid the production of useless fine grog and to procure a material of the necessary sharpness, the grog should not be ground in an edge-runner mill, but should be broken with a hammer or jaw-crusher until it will pass through a 2-inch hole, and then ground in a disintegrator (fig. 36A), between crushing rolls (fig. 155), or in a Hadfield's disc-crusher.

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[1] In 1913, L. Elborne and H. Godsal patented the use of a mixture of fireclay and china-stone (Cornish stone) for retorts.

[2] In Germany, old saggars from the porcelain works are extensively used.

[3] The lower figure corresponds to the minimum mentioned in the Standard Specification of the Institution of Gas Engineers.

K. Endell and W. Steger[1] have found that the binding clays should contain at least 95 per cent. of clay substance and the lean clays used for grog only 50 to 75 per cent. The normal refractoriness should be Seger Cone 28 to 34 (1630° C. to 1750° C.). Portions cut from the retorts should have a high tensile strength (50 kg. per square cm.), and should not deform more than 4 per cent. below 1350° C. under a load of 1 kg. per sq. cm. and preferably not below 1360° C.

Silica is mixed with clay as a substitute for grog for some retorts, particularly those used for refining siliceous ores, including some zinc ores. The most usual form of silica employed is a white sand, but flint clay or siliceous fireclay is sometimes preferred.

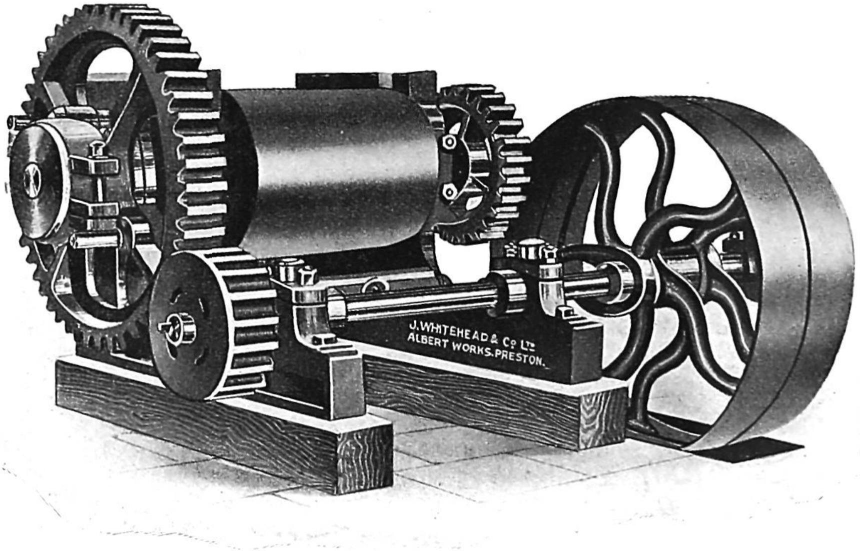

FIG. 155.—Crushing rolls.

The *clay* used to bind the particles of grog (or as the main material of which the retorts are made) is generally fireclay in Great Britain, but more plastic clays, bearing a resemblance to ball clays, are used on the Continent. The clay should have a refractoriness corresponding to Seger Cones 30 to 33, although this is not absolutely necessary, as some clays which soften at Cone 28, but have a long range of vitrification, are quite satisfactory. The shrinkage should be as low as possible, and the minimum porosity should be attained at about 1400° C. In order that the retorts may have a maximum resistance to any fluxes with which they may come in contact, it is desirable that the alumina content should be high. In special cases, however, materials have been used which contain very little alumina, as at the Sheffield Gas Works, but this is unusual. For metal-refining retorts, an aluminous material is almost essential. As the necessary properties are seldom obtained solely by the use of one clay, it is desirable to use several clays. In some localities (*e.g.* Stourbridge) these clays may be from the same mine, though at different depths, but in others clays of quite different properties are employed, *e.g.* kaolin and fireclay form a satisfactory pair.

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[1] *Metall und Erz*, 1923, **11**, 332–333.

The clay should be selected with great care, all obviously impure pieces being discarded. Iron compounds are particularly injurious in zinc retorts, as, at the temperature at which such retorts are maintained, fusible iron silicates and double silicates are liable to be formed, which not only reduce the refractoriness of the retort, but also cover the surface of the ore with a fused slag, making it impermeable to the reducing gases which are used to liberate the metal from the ore; hence, such silicates greatly increase the time and fuel required for the reduction of the ore to metal. Sulphides, if present, are decomposed—often with injurious results. The best method of removing impurities is by "picking"; washing and other methods of purification are, at present, impracticable. The selected and "picked" clay should be weathered, as described on p. 258, ground in an edge-runner mill, and screened, as described on pp. 264 to 270. As retorts are required to be very porous (in order to withstand sudden changes in temperature), it is desirable that the clay should not be too finely ground.

Coke may be added, if necessary, to the extent of 10 per cent. in order to produce a smooth surface and a denser material, as well as to facilitate the moulding of the retorts. It also reduces the contraction and enables a larger proportion of fine grog to be employed without much danger of cracking.

Carborundum may be added in some cases, especially where there is likely to be a considerable amount of abrasion. A. L. J. Queneau (Eng. Pat. 19,877 of 1905) recommends a retort having a special lining containing carborundum.

Proportions.—The proportions of the various clays and grog differ greatly, as they depend on the clays used. Among British retort manufacturers, a mixture of 6 parts of clay to 1 part of grog is quite usual, though the more progressive firms use more than twice as much grog, so as to have 30 per cent. of it in the mixture.

In Germany, gas retorts are usually made from—

(i) Grog which has been crushed in such a manner as to produce the most angular particles possible. A satisfactory mixture consists of 7 to 8 measures of grog consisting of particles 0·12 to 0·40 inch diameter, and 2 to 3 measures of grog consisting of particles 0·04 to 0·12 inch diameter. All particles which pass through a sheet having perforations $\frac{1}{25}$ inch diameter are rejected as too fine.

(ii) A mixture of 2 measures of highly refractory clay—preferably a kaolin or china clay, and 1 measure of highly plastic clay, equivalent to the Devonshire ball clay.

The proportion of clay and grog is varied so as to produce retorts of the maximum strength, whilst keeping the proportion of clay as low as possible. As the German retort manufacturers work with a more plastic clay, they are able to use as much as 10 parts of grog to 6 parts of clay for the best retorts, and equal parts of grog and clay for retorts of second quality. On the recommendation of Seger, many of them have long used a mixture consisting of finely ground kaolin 4 parts, finely ground plastic clay 2, pea-sized grog 8, pin-head grog 2 parts, for retorts of the best quality.

The use of mullite, prepared by heating a mixture of kaolin and quartz with alumina to above 1500° C., was patented in 1933 (Eng. Pat. 421,144).

Silica retorts are built of silica bricks and blocks of suitable shapes. These are made as described in Chapter III.

It has been found that retorts built of bricks made of silica bonded with clay retain the gas better than if lime is used as the bond.

Retorts for the distillation of zinc were formerly made in one piece like a crucible, but more recently large vertical continuous retorts made of bricks have replaced the smaller ones in many works.

The medium-sized and smaller retorts are usually made of fireclay and grog. They are made by hand-moulding or by mechanical pressing—seldom by casting, as shrinkage must be avoided as much as possible and a very dense body is regarded as important. When presses are used, the " clot " is made in a machine resembling a pipe-press and is afterwards given its final shape in a press of special design. As little water as possible must be used so as to ensure a dense retort. De-airing is highly advantageous.

The chief material used is Stourbridge fireclay, with a small proportion of grog made of the same clay. Some firms use Stourbridge fireclay, " Derby fireclay," and " Yorkshire pot clay " (p. 47) as well as grog. The retorts are usually given a very prolonged drying, so as to avoid all possible cracks. There is a tendency to use too little grog. That from old retorts is very suitable.

The retorts should be baked at about 900° C. before being used, so as to facilitate handling and to prevent loss of time in heating when in the furnace.

The best Belgian retorts for zinc distillation are made of a mixture of 39 parts of plastic fireclay, 12 parts of a leaner fireclay, 39 parts of siliceous grog, and 10 parts of coke. A mixture of silica rock and fireclay is sometimes used in making the grog, but ordinarily a siliceous fireclay grog is employed. The materials should be fairly coarse, and should be mixed and worked up very thoroughly, as zinc retorts require to have considerable mechanical strength. Some makers glaze their zinc retorts both inside and out with a mixture of blast-furnace slag and half its weight of washing soda, so as to make them more impervious. The addition of 10 to 20 per cent. of carborundum to the clayey mixture appears to be advantageous in increasing the thermal conductivity and durability of the retorts.

The properties of bricks for vertical retorts for zinc-distillation are described on p. 798.

The chief difficulty in making retorts for the distillation of zinc is to produce a dense retort which will not allow zinc vapour to pass through its walls, and to prevent the destruction of the retort (*a*) by the combination of zinc oxide, a spinel being formed out of the retort, and (*b*) by the action of the complex mixture of impurities in the ore. Sillimanite, bauxite, and corundum are less satisfactory in resisting this corrosion than fireclay.

The use of *magnesia* for retorts and muffles has been suggested by Steger, on account of its greater thermal conductivity, basic character, greater resistance to corrosion, higher refractoriness, and impermeability to zinc vapour. The application of a protective coating of zirconia or fused alumina and the admixture of carborundum with the retorts are worth further attention.

In lead works, where zinc is removed from crude lead by distillation, similar retorts are used, but there is less destruction by zinc. On the other hand, the corrosive action of the lead-silver alloy is very serious and necessitates the use of retorts very low in silica. A customary mixture is plastic clay 30 to 40 per cent., hard-burned grog with no free silica 50 to 55 per cent., and coke or graphite 10 per cent.

Mixing.—The clays and grog should be measured out in the correct proportions (there is an increasing tendency to use automatic measuring machines in place of the old-fashioned barrows and shovels), and spread out, moistened with about three-quarters of the total amount of water which will ultimately be required, and well mixed with wooden spades or with an open mixer of the trough type, provided with either one or two sets of blades. In some works, vertical or horizontal pug mills are used.

In order to secure the complete union of water and clay, it is best to leave the moist material for some time in the form of a heap or bed, and to turn it over several times or to put it through the mixer, it being considered that the longer the clay can stay in a moist condition, and the more mixing it undergoes, provided the treatment does not destroy the relative sizes of the particles, the better will be the final product. Should the repeated mixings cause an evaporation of some of the water, this must be replaced by an additional quantity; but the mass must always be kept as stiff as possible consistent with efficient working. The crudely mixed material is then passed through a pug mill. Where prolonged soaking is inconvenient, the clay should be mixed with at least its own weight of water in a blunger or similar mixer, and the resulting slip should be added to the grog, and the whole well mixed and then pugged.

It is important that the mass should not be too stiff whilst passing through the pug mill or it will not be properly mixed, and on this account it is often necessary to feed in a large quantity of water along with the clay mixture. As the mass must be made up into retorts in as stiff a paste as possible, the excess of water necessary for the proper working of the material in the pug mill must be removed before the mass is fit to use. This is accomplished by cutting the band issuing from the mill into blocks about 4 inches each way and setting them to dry on a warm floor. They must, of course, be frequently turned so as to dry evenly. When these blocks are so stiff as to be kneaded with difficulty, they are piled into a heap of about 2 yards each way (any excessively dry portions being damped), and the heap is beaten with wooden blades until a dense and compact mass is obtained. This is allowed to stand for at least forty-eight hours.

Some of the mixtures containing very fat clays should be passed through the mixer at least three times. The mixed mass is again allowed to stand, either in a heap or in the form of large balls, in order that it may "settle" and be as free as possible from internal stress and strain.

Treading the mass is still practised in some works, and has undoubtedly a great value in securing a homogeneous material, and where the cost of this treatment is not prohibitive it should not be omitted, but it should be in addition to, and not in place of, the mechanical treatment just described. In order to remove any chance air-bubbles in the clay, it is, immediately before use, wedged thoroughly by hand and beaten with wooden bats, or cut into thin strips and thrown violently on to an iron plate and made up into stiff balls by a kneading process.

The whole object of this great amount of working is to secure a stiff paste, which will be as even as possible in composition and through which the moisture shall be distributed with perfect regularity, so that each solid particle is in contact with its own share of water and all the air-bubbles are removed. Imperfect working has been found to be a frequent source of defects and to reduce the durability of retorts. In Germany, this method is closely carried out, though in England some of the stages are omitted for the sake of economy; this is undesirable.

The prolonged storage of the paste at various stages of its preparation is very important, as it has been found by numerous investigations that water will distribute itself through a clay paste far more evenly when left to itself than when mechanical mixing alone is used. It would, however, take too long if no mechanical mixing appliances were employed, and the combination of mixers and storing (or "souring") is found to give perfectly satisfactory results. The ordinary time allowed for this souring is fourteen to twenty-one days, the material being turned over four or five times in this period. If treading is practised, it may conveniently be done during the period of souring.

In order to use as little water as possible in the preparation of the paste, water-glass is sometimes mixed with the materials. This has the added advantage of giving the dried retort a greater strength, so that it is not so tender and is less liable to be damaged before firing.

Making the Retorts.—In England, the paste is softer and more plastic than that used in Germany, and, consequently, the shrinkage of the retorts is greater, with the result that there is more loss in manufacture.

The work which has to be done by the German makers is harder than similar work here, and it may be questioned whether many Englishmen would be willing to put in sufficient work to make the retorts from so stiff a paste. Notwithstanding this difficulty, there can be no doubt that the stiffer the paste the better will be the retorts made from it, provided the proper uniting of the particles is effected by the maker.

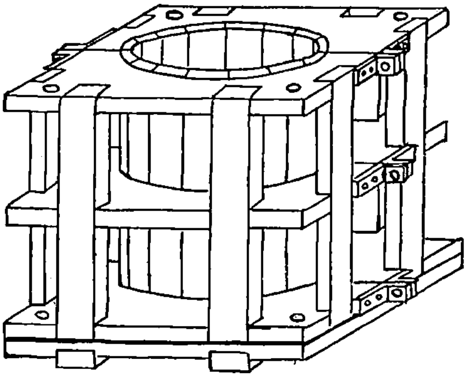

FIG. 156.—Retort mould.

Tubular retorts are made by hand, in wooden moulds, or by expression from a machine. The hand-made retorts are produced on wooden moulds or drums, each about one-sixth of the length of the retort, a sufficient number being used to complete the retort.

Three methods of hand-moulding are in use—

(*a*) *Outside moulding*, in which the paste is thrown on to the bottom and against the inside walls of the mould (fig. 156), thus forming a lining. This paste is then consolidated by repeatedly beating it with a wooden or plaster tool or with the workman's fists, and is then scraped until it is smooth and of suitable thickness. When the first mould is filled in this way and the clay has had twenty-four hours or more in which to stiffen, the mould is raised several inches, or a second mould is laid on the top, and a further portion of the retort is then made. This is continued until the retort is completed. A retort 6 feet 8 inches in length takes about twenty-one days to build, and though there are objections to the number of joints made by this method of building, very good retorts may be produced, provided due care is taken to prevent the joints becoming too dry before the next portion or "ring" is added.

(*b*) *Core moulding* is especially suitable for narrow, elliptical retorts. The core (fig. 157) is made of several pieces of wood. It is usually covered with zinc to facilitate its ready removal. Its exterior is precisely the shape of the interior of the retort. A slab of paste—the thickness of which corresponds to that of the end of the retort—is first made by rolling out or beating the material, as described on p. 677, and the core (previously oiled) is fixed vertically on this paste.[1]

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[1] Some workers make the closed end of the retort on top of the core and invert the whole before removing the core.

More paste is thrown on to and pressed against the core, its outer surface being smoothed and shaped by hand with the aid of profiles or gauges. Only the lowest portion of the core—about 18 inches high—is covered at first, a further "lift" of 14 inches to 18 inches being added after a few days. As each "lift" is added, a long scarfed joint is made, so as to form a continuous tube, and the lower part of each addition has to be dried partially before the next portion is affixed on top of it. Using this method, about the same time is required to make a retort as when an outside mould is used; the same objections apply to both these methods.

The thickness of the neck is increased by using a larger outside profile, and the bolt-holes are cut with the aid of a template when the retort is about half dry. To give the exterior of the retort the requisite smoothness, it is polished by the builder a few days after each "lift" has been built, and when finished the retort is usually washed over with a slip of ground clay and water, so as to give it a uniform colour throughout.[1] This method is similar in many ways to the use of an outside mould, but the position of the mould and paste is reversed.

(c) In *core and mould* making, both an outside mould and an internal core are used, great care being taken that the space between these is uniform. This is usually effected by bolting the core to the base-board of the mould in such a manner that the core is held firmly in position, but can be removed when desired. The mould is similar to that used for glass pots (fig. 152), but is much longer.

The paste is pressed into the space between the core and the mould by carefully ramming it with a spiked iron tool (fig. 107). When the space is nearly filled, a second part of the drum mould is added and the filling and ramming continued, these processes being repeated until the retort is complete. The retort must not be built too quickly, or it will not be strong enough. Hence, only a few inches should be added at a time to the retort. When the retort is completely made, the core is removed piece by piece, a pulley block and chains being used when necessary. The drums containing the retort are then lifted and turned to a horizontal position, and a boy or very slim man gets into the retort and smooths the inside of it by means of an iron scraper and a piece of leather or rubber. The drums and retort are then placed on a trolley and taken to the drying-room,[2] in which the drums are gradually removed and the outside of the retort is made smooth in the same manner as the inside.

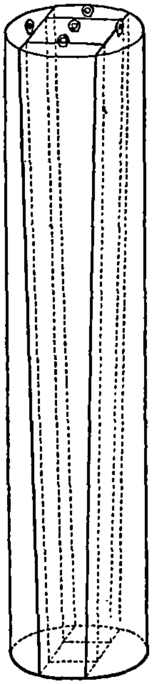

FIG. 157.—Core for retort mould.

In some German works, the pugged clay is cut into smaller pieces by a rotary slicer; these pieces fall on to a conveyor belt and are passed through a dryer, so that the makers are supplied with a coarse, slightly damp dust which is tamped into place by means of pneumatic hammers fixed to a standard,

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[1] See the paragraph on *the surface* of retorts near the foot of p. 686.

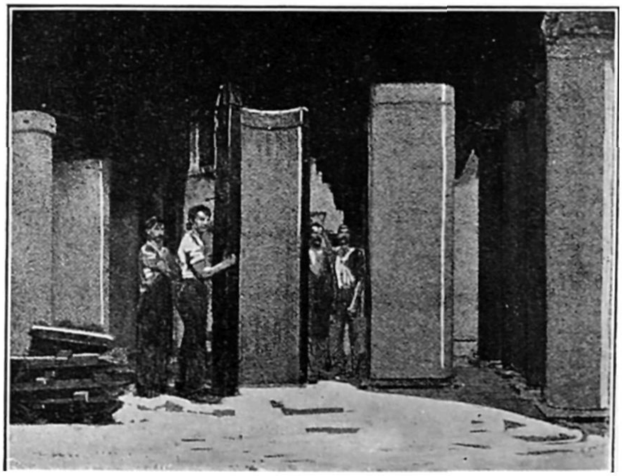
[2] Some firms dry the retort in the room in which it is made, so as to avoid the risk of breakage in transport. G. V. Evers (E. J. & J. Pearson, Ltd.), in 1913, patented the use of a kiln with a movable top or side and a travelling shaping machine which can make and deposit the retorts in the required position in the kiln.

the mould revolving slowly and being lowered as it is filled. This method of working is supposed to ensure an exceptionally uniform product.

The flange on the open end of most gas retorts is made by means of a special drum-mould which fits on the moulds used for the main part of the retort. The bolt-holes in this flange are cut after the drum-mould has been removed.

Careful and conscientious workmanship is always essential in retort making, as any carelessness or lack of thoroughness will inevitably show itself later. If the various "rings" of "lifts" are not properly joined to each other, the defects will show and can never be patched up satisfactorily, though some men are clever enough to sell defective retorts.

Machine-made retorts are produced in an expression machine similar to that used for saggars. The paste is fed into a vertical cylinder about 3 feet in diameter, fitted with a ram or piston having an 8-foot stroke. The lower end of the cylinder is fitted with an opening or die the size and shape of the outside of the retort and a core the shape of the inside of the retort. When steam is applied to the ram, the paste is forced out of the cylinder through the die in the form of a pipe of the desired cross-section. The flanged end of the retort is made first, by attaching an additional die to the machine; when this die has been filled with clay it is released and the remainder of the retort is then produced. The extruded "pipe" is received on a small wagon, carried on a counterpoise table which descends as the length of the "pipe" increases. When the wagon or bogie reaches the floor level, the retort is cut clear of the cylinder by means of a wire, and is then taken on the wagon to the drying-room. Ropes and battens are then lashed round it, the whole raised from off the bogie by a gantry travelling crane, and the bogie withdrawn. One end of the "pipe" is closed by hand, and bolt-holes are then made in the flange at the other end. The retort is then lowered so that one end rests on the floor. After a short time, the retort is finished by hand, any defects being remedied. A good machine of this type will make 400 feet of retorts per day.



(By the courtesy of Mr. T. A. Randall.)

FIG. 158.—Retorts after moulding.

It is sometimes more convenient to use a machine from which the extruded clay rises vertically, and to use hydraulic power so that the retort is subjected to a pressure of 1800 to 2000 lbs. per square inch. Such an arrangement is specially useful in the case of zinc retorts, which require to be exceptionally dense on the inner surface so as to prevent loss by the permeation of the volatile zinc through the pores of the retort.

Prior to 1914, such machines were invariably of Continental manufacture, but more recently machines supplied by Wm. Johnson & Sons, Ltd., of Leeds, have been used. These consist of a circular " clay chamber " closed at the top by a die and at the bottom by two hydraulic rams, one in the centre and a second annular one surrounding it. These rams are operated independently.

When the rams are in their lowest position the press head and die are swung aside, a large " ball " of clay is placed in the chamber, which it just fits, and the press head and die are then returned and locked in position. The central ram then gradually rises and passes through the mass of clay until it reaches within 1½ inches of the head. The second ram is next started, and causes the clay to be extruded past the die and " core former." The top of the retort is supported by a counterbalanced guide, and when a sufficient length has been extruded the mass is cut by a wire; the retort is then removed and taken to the drying-room.

Numerous patents have been granted for retort machines. Most of them are useless; the more successful machines are of the type just described or some simple modification of it, and need not be described in further detail. A portable retort-making machine is mentioned in footnote (2) on p. 679.

Although the mechanical production of retorts is apparently simple, it is found to be extremely difficult to make the larger sizes in this manner, so that it is usual to make only small and medium-sized retorts by machinery.

The fact that the machine-made retorts are produced in a single operation may account for somewhat greater homogeneity, but the gradual building-up in distinct lifts ensures the slow drying which is so desirable. Machine-made retorts are denser and heavier, unless the excess of density is destroyed by the addition of sawdust or coarser grog. Owing to the high working pressure of the machines, the prepared clay must necessarily be stiff, otherwise warping and sagging will occur after the material has passed the die. Stiff material when shaped by pressure is not so effective for most purposes—particularly retort work—as a more plastic clay paste which is moulded by hand. When the clay is plastic, the additional amount of water is afforded an opportunity of carrying out its function of knitting and binding the particles. Moreover, when the ram, under heavy pressure, squeezes or drives the clay out of a retort machine, there is a tendency to destroy the setting of the " grog " and to drive the coarser particles together, forming patches or " pockets." On the other hand, a machine-made retort prepared with due care is far cleaner, more regular, and straighter than one made in successive lifts by hand.

Casting retorts in plaster-lined moulds, using a suspension or slip, was first attempted in 1917 and has been successfully used ever since, though its commercial use did not commence until 1920. The chief advantages of this method of production are: (i) the density and grog-content can be varied as required; (ii) the retorts can be dried much more rapidly than modelled or hand-moulded retorts; (iii) the retorts can be burned more rapidly; and (iv) much less skill is required in their manufacture. B. J. Allen has suggested casting gas-retorts by applying a vacuum to the moulds, and this has proved very advantageous. The process of slip-casting is described more fully in Chapters XII. and XIII.; it seems unnecessary to describe the simple variations needed when this process is applied to retorts.

Finishing.—By whichever way the retorts are made, it is most important that they should be carefully finished, as any irregularities on their internal surface facilitates the decomposition of the hydrocarbon gases in retorts used for gas manufacture, and results in the deposition of carbon. The smaller amount of deposition of carbon in iron retorts is partly due to the smoothness of their surface and partly to the absence of a catalytic action of fireclay on carbon monoxide, which results in the separation of carbon. If the retorts are glazed this difficulty is largely overcome. In the case of retorts used for zinc and other metals, a smooth surface is desirable to prevent excessive corrosion by slags in the charge.

Drying.—Retorts are dried in sheds, the temperature of which is not allowed to rise above 25° C. (75° F.). These sheds are heated by coke stoves some distance away from the retorts or, preferably, by steam-heated flues beneath the floor. Usually, the drying floors are heated by exhaust steam from the engine, with a little live steam going through the pipes at night. The objection to coal-fired stoves is that the temperature inside the shed is subject to such quick changes that the goods may be damaged. The floor should be divided into independent sections, each controlled by a separate steam-cock, so that the temperature in each part of the floor may be regulated. Careful drying and handling are essential. If any part of the retort is subjected to a draught, however slight, it is liable to cause a crack and the retort may be irretrievably damaged. It is, consequently, necessary that the drying should take place in rooms perfectly free from draughts, and it is better to have a series of small rooms, each holding a few retorts, and to close them as soon as they are full, rather than to employ large rooms in which the men are constantly moving about and in which there is always a current of air. There is much scope for improvement in the drying of retorts, and some of the methods used for other goods, and described in other chapters, may advantageously be adopted. Thus, the use of small chambers which are kept closed and the air in them saturated with steam until all the retorts have reached a temperature of about 120° C. is beneficial. In these chambers, no drying is allowed to take place until the retorts are quite hot; rapid drying is then safe.

The use of steam injected into the air of a large shed is advantageous, but it is not so good as using a small chamber.

The outsides of the retorts dry naturally by radiation; the insides do not usually receive special attention, though in some works a gentle current of air is forced into them by means of a fan. A very primitive method—still used in some works—consists in lowering into the retort an iron " fire-basket " about 5 inches wide, filled with burning wood and attached to a chain and continually moved up and down inside the retort so that the heat is not too intense at one spot. This method, whilst occasionally useful, is not really satisfactory, as there is more danger of cracks due to excessive heating, and it is far preferable to blow or draw warm air through the interior of the retorts by means of a fan, as by this means the temperature is more uniform and more easily regulated.

In every case, the drying of the retorts ought to proceed very slowly—from two to three weeks being usually necessary—the same precautions being taken as for glass pots, though the drying is less tedious. Some manufacturers prefer, when possible, to allow the retorts to dry naturally, making them early in the spring so that they may be drying during the warm days. When this is impracticable, however, they employ artificial heat for drying the retorts.

When dry, the retort is raised by a crane, or lifted, on to a bogie truck and conveyed to the kiln.[1] It is placed in position, again lifted, the bogie

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[1] See footnote (2) on p. 679.

is withdrawn, and the retort is finally deposited on its end on the floor of the kiln. The burned retort is removed in a similar manner.

Kilns used for burning retorts are generally of the down-draught type. They may be either rectangular or circular in plan and may, preferably, have a movable top, which may be lifted off to facilitate the setting of the kiln.[1] A convenient size of kiln is 26 feet by 10 feet by 15 feet high.

Sometimes the kiln has a perforated floor, but ordinarily the floor is solid, with one or more " well-holes " leading to the main flue. This is unfortunate, as the heat is less uniform than in a kiln with a perforated floor. The chief advantage of a solid floor is that it is stronger and facilitates the setting.

Gas-fired kilns are seldom, if ever, used for retorts in Great Britain; on the Continent, several are employed for this purpose.

Generally a temperature of 1250° C. to 1400° C. (corresponding to Seger Cones 8 to 14) is attained in firing the retorts; in order that retorts may conform to the Gas Engineers' Standard Specification the temperature in the kiln should exceed 1400° C.

Setting.—Gas retorts are placed vertically in the kilns on a bed of grog or white sand. They are placed as close together as their flanged ends will permit. If there are not sufficient retorts to fill a round kiln, the retorts may be placed in a ring between the bags and the centre, the remaining space being filled with firebricks, etc. In a rectangular kiln, the retorts are best placed near the centre. Very great care and skill are needed in setting or the retorts will fall.

Burning.—The kiln must be heated very slowly in order to avoid cracking the goods, and the fires should not be increased until all steam has ceased to issue from the chimney. The final temperature to be reached in the kiln should be higher than the retorts are likely to attain when in use, so that no further shrinkage will occur. The finishing temperature varies greatly in different works, but to comply with the requirements of the Gas Engineers' Specification it must be above 1350° C. (Seger Cone 12); actually it should be about 1410° C. (Cone 14).

The fuel consumption is very heavy (averaging 6 to 8 cwts. per ton of retort fired), this high figure being chiefly due to the fact that in the kilns employed the greater part of the heat in the fuel escapes up the chimney.

The fuel consumption varies according to the dryness of the goods, their thickness or " cubic contents," their shape and " setting," and the quality of coal used.

By using a continuous kiln the fuel consumption could be greatly reduced, but in many works the output would not justify a continuous kiln.

The period of burning, including steaming and cooling, takes from ten to eighteen days, according to the class of retorts being burned and other circumstances. The heating must be very slow, as the retorts are very sensitive to sudden changes in temperature before they have been burned. For the same reason, the retorts should be shielded from the direct action of flame. In some parts of Great Britain, it is by no means uncommon for a retort to stand in the kiln for several weeks, yet at the end of this time its temperature will be under 500° C. If it is made of clay of the right-sized grains and the correct stiffness, there is no need for this time-wasting storage in the kilns. It is only when the retorts are made of too fine a mixture or from too wet a paste that such excessive storage below 500° C. becomes necessary, and as retorts made from these materials will be of short durability in actual use,

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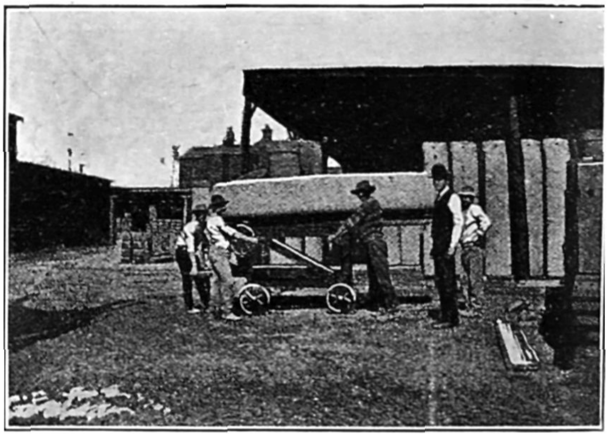
[1] See J. Morton's patent (1891) and G. V. Evers' patent (1913), p. 679.

the manufacturers concerned should reconsider their method of preparing the materials.

The end of the firing may be judged by Seger cones, by measuring the shrinkage of the retorts, or by removing small glazed trial pieces from the kiln at intervals. In the last method, when the glaze is properly matured and glassy, the kiln is regarded as finished.

Careful burning is almost as necessary as careful drying, though there is less liability to damage in the kiln than some people suppose. If the defective retorts are carefully examined, it will be generally found that the damage has been done by sending the retorts to the kiln before they have been properly dried, or to their having been spoiled in some other way before they reached the kilns rather than afterwards; such defects obviously ought not to be laid to the fireman's charge.



(By the courtesy of Mr. T. A. Randall.)

FIG. 159.—Taking a retort to the kiln.

Cooling.—The cooling of the kiln must be as carefully watched as the firing, or the retorts will fly to pieces. The best methods and rates of cooling can only be learned by experience, and no general description can be given. The greatest care is needed in opening the kiln to facilitate the cooling, as this has a tendency to introduce draughts and so crack the goods. A good method is to allow the kiln to cool fairly rapidly to a dull red heat (about 850° C.), and after this to cool it very slowly, and not to open the kiln until the contents are below 30° C.

Glazing.—In order to render retorts impervious to gases, some firms cover the interior with a mixture which fuses to a glaze when the retorts are fired. The glaze is useful at first, but in gas manufacture it soon becomes unnecessary, as the *scurf* or *retort graphite* which forms on the inner surface of the retort soon renders the latter impermeable. Moreover, the glaze cannot withstand the repeated heating and cooling of the retorts, and it therefore crazes, cracks, and peels off. There are, however, obvious advantages to be derived from a thin coating of felspathic glaze, and, as the cost of glazing is only trifling, it should receive the careful consideration of those firms of retort manufacturers who have not hitherto adopted it. The chief advantage of a glaze is that it prevents much leakage of gas from the retort during the time which elapses between its first being used and that at which it is lined with deposited carbon.

Salt glaze is not altogether satisfactory, though popular amongst certain Continental makers. Its chief disadvantage is that it is apt to penetrate too far into the material of the retort and act as an internal flux rather than as a glaze—an objection which cannot be urged against felspathic glazes.

The ordinary mixtures of red lead, flint, and clay used for coarse pottery are useless for retorts, as such glazes craze too readily.

A suitable glaze consists of felspar to which nearly half its weight of whiting has been added. To this is added enough china clay to make it adhesive before it is burned. The usual limits for the composition of such glaze are—

Felspar	100 lbs.
Whiting	42 ,,
China clay	30 to 110 lbs.
Flint or sand	65 to 250 ,,

corresponding to the formula—

$$\left.\begin{matrix}0{\cdot}3K_2O\\0{\cdot}7CaO\end{matrix}\right\}0{\cdot}5\text{—}1{\cdot}0Al_2O_3,\ 4{\cdot}0\text{—}10{\cdot}0\ SiO_2.$$

The average between these limits is used by several firms, who finish burning the retorts at Cone 14.

Glazes to work at lower temperatures can also be used, but it must be remembered that, other things being equal, that will be the best retort which has been fired at the highest temperature. A popular retort glaze has the following composition, and corresponds to Seger Cone 4 in composition, but must be fired at Cone 9 or above to give satisfactory results:—

Felspar	28 lbs.
Whiting	12 ,,
Kaolin or china clay	17 ,,
Sand or flint	43 ,,
Water	10 gals.

This glaze is quite the best that can be used by firms not wishing to finish at so high a temperature as the first-named; but even this necessitates heating the kiln to a much higher temperature than is, at present, customary.

S. A. M'Minn (Eng. Pat. 137,419—1919) has patented the use of a mixture of 30 per cent. or more of powdered glass and a fireclay or china clay, or a mixture of equal parts of china clay, siliceous clay, and glass as a glaze. The glaze must, of course, be adjusted to the composition of the retort.

As it is not necessary that the glaze should be white—the colour being of no importance—other cheaper materials may replace those just mentioned.

A useful and particularly cheap glaze discovered by Moore and Mellor consists of:

Soft Cornish stone	85 parts
Limestone	15 ,,

This glaze matures at Seger Cone 8.

There is no need for the glaze to be quite transparent; on the contrary, the semi-opaque glazes are often preferred, partly, no doubt, because they give a superior finish to the interior of the retort, and do not show the iron spots so much as when a transparent glaze is employed.

The glaze materials should be finely ground, mixed in the required proportions, and made into a cream or slurry by the addition of rather less than their weight of water. In order that it may adhere more closely to the retort before firing, it is well to add some material of an adhesive nature to the glaze slip. The most popular material for this purpose is dextrin or gum arabic, but powdered glue may also be used. Glue has several advantages, one of which is that it enables an exceedingly thin layer to be painted on if the glaze is first made into a solid jelly.

The glaze is applied to the retorts with a brush or spray, care being taken not to use it so roughly as to damage the retort. A long-haired painter's brush which has had the handle cut off, leaving a stump of only a couple of inches or less in length, is most suitable and least likely to do damage. If necessary, several coats of glaze may be put on, though more than three should usually be avoided.

Retorts used in the distillation of some metals gradually acquire a natural glaze in the course of working, which makes the application of a glaze to the interior of the retorts largely unnecessary. In some cases, however, an artificial glaze has the advantage of preventing the corrosion of the retort which occurs when a natural glaze is formed. Thus, if an effective felspathic glaze is used in a zinc retort, the durability of the latter is prolonged. In an unglazed retort, the zinc vapours gradually attack the inside, forming zinc aluminate (zinc spinel) and converting some of the quartz into tridymite, thus greatly shortening the life of the retort.

Retorts should not be glazed externally, as this reduces their durability by permitting flue-dust, etc., to adhere to and eventually combine with them, though the formation of a glaze when a retort is in use cannot always be prevented.

Patching.—Should the retorts be slightly cracked, yet not sufficiently so as to be unsalable, they may have the cracks smeared over with a mixture of felspar and water-glass or grog to which a little borax has been added; but this treatment can never make a damaged retort into as good a one as a retort that is free from cracks, and should never be used when avoidance is possible.

Lining.—Instead of glazing, the inside of retorts may be lined with some other material so as to make them impervious or more resistant to the action of the charge. For example, retorts may be lined with a stoneware clay of a readily vitrifiable mixture, such as equal parts of fireclay and china stone. This vitrified material renders the retort impermeable and is less liable to craze than is a true glaze. Retorts may also be "lined" by dropping gas tar or oil into them whilst they are in the kiln. The heat decomposes the hydrocarbons, and the carbon set free fills the pores near the surface of the retort. A modification of this process, patented in 1911 by R. Lessing, consists in heating the outside of the retort and exposing the inside to hydrocarbon vapours; a carbonaceous deposit is thereby formed which fills the superficial pores. C. H. Wilden, in 1891, patented the application of a paste, made of molasses or treacle with plumbago, to the inside of the retort.

Other linings are (*a*) water-glass, with various inert additions, (*b*) magnesia, and (*c*) a mixture of magnesia and silicate of soda, such as that patented by H. J. Hadda in 1900.

It has been suggested that a thin coating of zirconia or bauxite should be applied externally to retorts so as to prevent the formation of superficial cracks. Both these, however, have disadvantages, as zirconia is a very poor conductor of heat and readily peels off a clay retort, whilst bauxite is very liable to form a spinel if applied to a zinc retort. Carborundum might be advantageously employed.

Properties of Retorts.—Retorts should have the following properties:—

(i) Ample resistance to unavoidable changes in temperature (p. 691).

(ii) Sufficient porosity to enable them to resist thermal shock, yet without making the retorts unduly weak (see *below*) or unduly permeable to gases (p. 688).

(iii) Sufficient resistance to abrasion by the contents and by the gases used to heat the retorts (p. 695).

(iv) Ample mechanical strength (p. 689).

(v) Ample refractoriness (p. 690).

(vi) Sufficient resistance to corrosion (p. 692); this usually involves a suitable texture (see *below*).

(vii) High thermal diffusivity, or rate of heating, with a minimum fuel consumption (p. 696).

The *shapes* and *sizes* of retorts have been described in the preceding pages; they must be reasonably close to the dimensions ordered.[1] The *colour* is unimportant, but is usually buff to light reddish brown. It should be as uniform as possible, and there should be no black heart or core, as this indicates too rapid a firing during manufacture. The higher the finishing temperature and the more prolonged the firing, the darker will be the retort. Most retorts which have been properly burned show numerous spots of black iron silicate. These are due to the pyrites in the clay having been imperfectly removed.

The *surface* of a retort—both inside and out—should be smooth and free from flaws or joint-marks (" winding "). All efforts to improve the appearance of the retort by washing it over with slip should be avoided.

The *texture* of a retort—that is, the coarseness or fineness of its grain—has a considerable influence upon its physical properties. For high refractoriness, a coarse-grained retort is required. For mechanical strength and heat conductivity, on the contrary, a close-grained and dense substance is necessary. Hence, it is impossible to attain an ideal texture for a retort, because some of the conditions require porosity and others necessitate a material of high density and close texture. These contradictory requirements have to be reconciled as far as possible; special attention is usually given to the effect of heating and cooling, with the result that modern retorts are manufactured with a decidedly coarse grain. (In 1911 Gas Engineers' Specification,[2] " no grog shall be used which will pass through a standard sieve having sixteen meshes to the linear inch.") Sufficient clay must be present to bind the coarse grains of grog together or the retorts will be weak, friable, and liable to contain fissures and cracks.

The texture of a good retort is that of coarse particles of grog united and surrounded by much smaller particles of clay, the whole mass being as uniform and porous as possible and without holes or fissures. This uniformity of texture tends to increase when the retort is in use, as the clay and grog grow more like each other and eventually form an almost homogeneous mass. The material should be of moderate hardness, though this is of minor importance.

The *apparent porosity* should be high, to enable the retort to withstand repeated heating and cooling, but as high porosity is detrimental to the strength of the retort and to its resistance to fluxes, ash, etc., it is necessary to avoid a porosity much greater than is required for providing resistance to changes in temperature. Retorts with 30 per cent. porosity, made by several British manufacturers in 1912–13, were too weak to be used. This may have been

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[1] A frequent complaint of engineers is that British retorts are less accurately dimensioned than those bought abroad.

[2] This proviso is omitted from the last (1934) Specification.

partly due to an excessive porosity or, more probably, to the use of too coarse a grog, but it shows that mechanical strength and porosity must be considered together.

The most generally satisfactory method of increasing the porosity of a retort material is to use (*a*) coarser grog, or (*b*) a larger proportion of grog, but in order to get the best results, both the size of grain and the proportion of grog must be adapted to the clay used. There is room for further investigation as to the best porosity for retorts, as the only standard at present recognised is that for gas retorts made under the Gas Engineers' Specification, which stipulates that the porosity shall not be less than 18 per cent. by volume. It is interesting to note, however, that many German retorts have a porosity of 25 per cent., and a small proportion of large grains of grog. The defects in many retorts made in accordance with the Gas Engineers' Specification are due to the use of too coarse a grog and of an insufficiently graded material. Many British retort makers have not realised that grading is as essential for retorts as it is for firebricks.

The *impermeability* of a retort to gases is important if a serious loss of the vapour or gas produced in the retort is to be avoided. To secure impermeability it is usually sufficient to glaze or line the interior. Some engineers consider glazing unnecessary, and that the dust and scurf [1] in the retort soon make it impervious; hence, this subject has not received as much attention as it appears to deserve. In retorts for refining metal, an increase in the tension of the gas increases the amount passing through the walls and decreases the amount of gas passing out of the condenser. The loss of metal increases with an increase of pressure in the retort, so that this must be very carefully controlled in order to avoid loss.

The *expansion* and *contraction* which retorts undergo when in use are liable to cause serious cracks. In the case of fireclay retorts a noteworthy expansion or contraction is a sign of imperfect manufacture and particularly of insufficient burning.

A silica retort, when heated, may undergo three changes:

(i) Expansion and contraction on heating and cooling. In a well-burned silica retort, three-quarters of the total expansion (0·9 per cent. linear) occurs below 300° C., *i.e.* well below a dull red heat; after this is completed the heating may be more rapid.

(ii) A reversible expansion due to the inversion of one form of silica into another (p. 163).

(iii) An irreversible expansion due to an increasing formation of cristobalite or tridymite whilst the retort is in use.

These changes can create strains in the retort which weaken and may destroy it, unless the retort is heated very cautiously and equal care is used during the cooling.

Constancy of volume is best obtained by using only materials which have been sufficiently burned before use. Even then, silica retorts tend to " grow " as a result of the slow conversion of unaltered quartz into cristobalite or tridymite.

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[1] This scurf is formed by the decomposition of the coal-gas and tarry matters with the liberation of free carbon in the pores of the retort. Carbon may also be deposited in the pores of fireclay from various volatile carbon compounds which are decomposed by heat, particularly in the presence of a porous material like fireclay, and carbon is one of the products of the decomposition. The deposition is often more intense in the presence of hydrogen, as this combines with the oxygen in the carbon compounds and facilitates the decomposition of the latter. The formation of a deposit of carbon is particularly marked in the presence of carbon disulphide, carbon monoxide, and some hydrocarbons.

The *growth* of silica retorts is due to the conversion of quartz, which was unaltered in the burning, into cristobalite or tridymite when the retort is in use. The expansion may be very serious and may cause much cracking. The remedy is to use only silica retorts which have been adequately burned, so that the specific gravity does not exceed 2·36.

Both expansion and shrinkage in use are serious defects, the latter especially so. They can only be avoided by burning at a sufficiently high temperature for a sufficient length of time. As a rough guide, the fifth clause in the Gas Engineers' Specification is useful; this is a modification of Wedgwood's pyroscope, and provides that a piece of retort, when re-heated to a temperature of Seger Cone 12 (1350° C.) for two hours and allowed to cool, shall not expand or contract more than 1 per cent. of its original length. The weakness of this test lies in the fact that it is the volume of the retort *when hot* which is important, yet on this point the test gives no indication; it is, however, of value as showing whether a particular material has been sufficiently fired.

The author has long held the opinion (amply confirmed by an extensive practice) that for the best work no retorts or blocks should ever be used which have been fired in the kilns at a temperature of less than 1350° C. Notwithstanding the statement of many makers to the contrary, there is no serious difficulty in obtaining this temperature with most retort-kilns now in use, and the increased durability of the product and great reduction in cost of repairs and renewals amply compensate the users for any slight additional cost which may be incurred in firing the retorts to the higher temperature.

It is also important, before condemning retorts for excessive shrinkage, that the mason's work shall have been properly carried out. It is not unusual to find that condemned samples do not shrink excessively when heated alone, but that the real defect is due to the use of very thick joints in the masonry.

Mechanical Strength.—Retorts must be sufficiently strong to resist deformation under any pressure to which they may be subjected at high temperatures, including the intrinsic strength necessary to enable them to retain their shape when supported only at each end.

The mechanical strength of a retort is usually judged by the resistance of a piece of it to a crushing force, expressed in lbs. per square inch. As generally carried out, the crushing strength is of little value, because it is measured on the cold material, whereas far greater importance should be attached to the strength of the retort at the highest temperature it is likely to reach when in use. The mechanical strength of a hot retort is much less than when the retort is cold, on account of the vitrified matter becoming more or less fluid (viscous) at the higher temperature.[1] The loss of strength increases with the temperature and also with the pressure applied to the retort, and is much more noticeable with fireclay retorts [2] than with those made of silica. The fireclay retorts yield gradually when heated under a load, but the silica retorts collapse suddenly at a higher temperature. So long as the softening is not appreciable at the temperature at which the retorts are used it is unimportant,

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[1] Compare the mechanical strength of hot bricks under a medium load, as described in Chapter II.

[2] The internal strains set up in retorts in which coal or oil is heated are of a different character and are presumably due to the carbonaceous matter absorbed in the pores of the retort. It is well known that some carbon compounds are decomposed by heating in contact with fireclay in a manner quite different from that which occurs when the same compounds are heated in contact with silica; the exact nature of the decomposition has not been exhaustively studied. It appears to be catalytic and due to the chemical composition of the fireclay. The carbon deposited in the pores of fireclay retorts is seldom as detrimental to the strength of the retorts as is sometimes supposed, though, in some instances, it has unquestionably reduced the durability of such retorts (see footnote on p. 688).

but it should always be borne in mind in designing retorts and settings and in determining what materials to use in their construction. There is a curious belief among many engineers, who—assuming that, because the proportion of silica is usually the largest of all constituents, it must, therefore, be the most important—are apt to measure the value of a material by the proportion of silica it contains, whereas, in reality, they should proceed in an almost contrary direction, as, beyond a certain (not well-defined) limit, any additional silica only detracts from the refractoriness *per se* of the clay. In reality, any relationship which exists between the refractoriness and the composition of a retort material must be due primarily to the *clay* it contains and only indirectly to the alumina, silica, or any other oxides. In this connection, it must always be remembered that a comparatively small amount of flux will seriously reduce the refractoriness of the material.

The maximum load in the settings varies with the different types of plant from 12 to 28 lbs. per square inch, and the temperatures at these points of maximum load vary from 1100° C. to 1400° C. The maximum temperature to be expected under abnormal conditions is given by several observers as 1650° C.

The *refractoriness* of a retort should, strictly, refer to its ability to stand slow heating to a high temperature, but the term is often used to indicate its durability under various conditions of use, including those which involve rapid changes in temperature and the effect of flue-dust and other corrosive substances.

The Gas Engineers' Specification requires that a piece of retort shall show no signs of fusion after it has been heated in an oxidising atmosphere to a temperature of not less than that needed to bend Seger Cone 28 (about 1630° C.), the heat being increased at the rate of 10° per minute. A more usual test is to cut a piece of retort to the shape of a Seger cone and to insist that it shall not bend when heated under conditions where Seger Cone 30 bends until its apex is just level with the base.

The rate at which the material is heated has an important effect on the temperature at which fusion will occur, prolonged heating at a low temperature having a similar effect to a shorter heating at a higher temperature.

The refractoriness of a retort, in the strict sense, depends on that of the clay and grog used in its manufacture, but when the term is used broadly, to indicate heat-resistance in actual use, it is almost impossible to define the conditions which affect it, so numerous and complex are they. Hence, it is necessary to subdivide them into groups and to study these separately.

The *fusibility* of retorts (apart from that caused by impurities in the materials) is usually brought about by flue-dust or by fluxes in the contents of the retort (see *Corrosion*), but it is increased by a reducing atmosphere around the retort. With care, however, a reducing atmosphere may be avoided and this defect prevented.

In some cases, the use of an unsuitable fire-cement will effect a partial fusion of a segmental retort (see Chapter XVII.).

The fusibility of retorts, like that of firebricks, is affected by the pressure to which the material is subjected when heated. Brown and Montgomery have found that some good material softens sufficiently to lose its shape when heated under a load at a temperature of only 1300° C. and, more recently, J. W. Mellor has found that the fusing-point of fireclay bricks is lowered about 200° C. when they are heated under a load of only 54 lbs. to the square inch. For further details see p. 355.

It is interesting to compare these temperatures and pressures with those given under "Mechanical Strength" and in the following table :—

TABLE XCIV.—SHOWING TEMPERATURES OF GAS-RETORT SETTINGS.

	Furnace.	Combustion Chamber.	Interior Carbonising Chamber.	First Pass Waste Gas Flue.	Second Pass Waste Gas Flue.
° Fahr. .	1600 to 2400	1600 to 2700	1500 to 2400	1300 to 2200	570 to 1600
° Cent. .	870 „ 1315	870 „ 1480	815 „ 1315	705 „ 1205	300 „ 870

Resistance to sudden changes in temperature is always difficult to secure, though porous retorts are less sensitive than dense ones (see *Porosity*).

Ability to withstand sudden changes in temperature is specially needed in gas manufacture, where a retort full of almost white-hot coke is suddenly emptied—the fall in temperature inside the retort being particularly rapid, whilst the outside of the retort remains at a practically constant temperature. There are thus set up a number of violent strains within the material of the retort and, unless its texture is suitable for permitting these strains, the damage done may be serious. The amount of strain produced will depend upon the relative freedom of the various particles composing the retort or block, and this freedom to expand or contract may be in part influenced by such extraneous conditions as the "setting." The study of the effect of sudden changes in temperature is thus highly complex. Omitting for the moment the difficulties due to defective setting, however, the amount of strain produced within the article itself will be, roughly, proportional to the coefficient of expansion of the material and will be inversely proportional to the pore-space. Hence, such strains will be far greater with dense articles than with more porous ones.

Small external cracks on the surface of retorts are always produced on setting a retort in a hot furnace and when a cold charge of fresh material is thrown into a heated retort. These cracks are usually too small to be serious; most of them heal quickly by the deposition of soot or slag when the retort has been in use for a short time. If necessary, they may be repaired by means of a mixture of 50 parts of carborundum and 50 parts of clay.

"Mouth cracks" in retorts which extend partly or wholly through the material of which the retort is composed are chiefly due to the mouth receiving less heat than the centre; they can seldom be wholly avoided.

Any degree of porosity (within reasonably wide limits) may be given to articles made of clay by the addition of materials which will burn out during the firing, leaving pore-spaces in their place. The disadvantage of this method of increasing the "life" of retorts is twofold. The greater the porosity of the retorts, the more are they liable to cause wastage of gas through the walls, and the more air there is in the pores of the material, the slower will be the retort in heating. Consequently, the retort manufacturer is in a dilemma. If he makes a retort which is sufficiently porous to be very durable under sudden changes of temperature, he will receive complaints that his retorts take too long to heat up; while if he attempts to produce retorts that can be heated rapidly, he runs great risks of manufacturing articles which will only last a short time.

In such a case, compromise is essential. If gas engineers look for rapidity in heating, they must be prepared to forego some amount of durability. Fortunately in some respects, though disadvantageously in others, a retort soon becomes covered internally with a coating of deposited carbon which stops up many of the pores, and so renders satisfactory what would otherwise be an unusable porous retort. Hence, the modern manufacturer aims at producing retorts which are really very porous when new, as he is fully aware that the deposited carbon will rapidly prevent them from leaking excessively. In this way, it is possible to obtain all the advantages of resistance to sudden changes of temperature combined with sufficient gas-tightness for all practical purposes. Such retorts are, however, relatively bad conductors of heat and thus take more time and fuel to raise them to the temperature necessary for the coking of coal, though the difference in this respect is seldom of more than academic interest and the cost of the extra fuel is far more than counterbalanced by the saving in retorts and in re-setting.

Flaking or *scaling* of the interior of the retort may be due to deposited carbon (*scurf*), to volatilised alkalies, to sudden changes in temperature, due to irregular downward movements of the charge, and to damage done by pokers or rods. Where flaking is most serious, dense bricks of low porosity should be used.

Holing may be due to slag or to the leakage of gas through a crack or opened joint. As the gas passes through to the combustion chamber, it ignites and burns with so intense a flame that the size of the hole is rapidly increased.

The *acidity* of the material forming a burned retort is important in relation to the salts present in the coal or other contents of the retort and the flue-dust from the fuel used for heating it. Like all goods made of burned clay, hot retorts have strongly acid properties and combine readily with bases and salts, with the result that, under some conditions, they are soon destroyed.

This *corrosion* of the inside and outside of the retorts must be considered separately. The *internal* corrosion is almost invariably due to metallic oxides and salts in the contents of the retorts. In the distillation of zinc and other metals, the corrosion is chiefly due to metallic oxides combining with the clay of the retorts, but in the case of gas retorts the corrosion is caused by chlorides, sulphates, and carbonates in the coal,[1] and to some extent to the carbon deposited in the pores of the retort during distillation. In addition to sodium salts, there is always a little iron oxide, with some carbonate of iron, and a variable amount of silica and silicates.

All these compounds may be divided into three groups, as far as their action on the retorts is concerned: (*a*) decomposable salts, (*b*) free bases, and (*c*) direct-acting salts.

The *decomposable salts* are those which, when heated in contact with a stronger acid, are split up into a base and acid, the base uniting with the stronger acid and setting the weaker one free. Thus, calcium sulphate is decomposed into calcium oxide (lime) and sulphuric acid; common salt is decomposed into soda and hydrochloric acid. The soda and the lime combine with the strongly acid fireclay, forming a fusible silicate (resembling " salt-glaze "), and the volatile acids are set free.

Many coals contain alkali chlorides and compounds of iron which are volatilised during carbonisation. These form the chief cause of corrosion and the formation of " sticky spots " to which the charge adheres.

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[1] It is erroneous to attribute the corrosion solely to common salt (sodium chloride), as there are other salts present in coal which may be equally destructive. The percentage of soluble salts in a coal does not always indicate the amount of corrosion which will occur. Indeed, coals differ greatly in their corrosive properties; those from South Yorkshire, North Derbyshire, and Stoke-on-Trent have a serious action. Welsh coal does not usually corrode retorts in this manner.

Ferrous oxide in the retort material, or in the coal, is also a prominent cause of corrosion; it may be produced from ferric compounds by the reducing conditions in the retort.

The *free bases*, such as oxide of iron, lime, etc., combine directly with the fireclay, and form fusible silicates, which act like those just mentioned.

The *direct-acting salts* behave like the free bases, but are less powerful and much slower in their action, though the final product is similar to that with the bases. The most important of the direct-acting salts are the complex silicates, such as mica, felspar, etc.

In each instance, the new compound formed is much more fusible than the original clay or silica, and it gradually falls away, leaving gaps or flakes.

It is important to note that the presence of moisture is necessary in order that the clay or silica may react with the decomposable salts; hence the use of damp coal has a corrosive action on retorts, because the moisture present in the coal is a valuable assistant in facilitating the reaction between the clay or silica and the salts.

The speed of reaction between the salts in the coal or coke and the clay or silica of which the retort or bricks are made depends more on the physical state of the materials than on any difference between the composition of a silica or clay retort.[1] The compounds produced with silica are more fluid and fuse more readily than those with clay, but the difference between the two is not more than is readily masked by variations in the size of the particles used for making the retorts. When finely ground clay or silica is mixed with common salt, the silica mixture melts more readily than the one containing clay, but if the clay and silica are burned before use and then crushed so that only grains $\frac{1}{25}$ inch diameter are used, the reaction is slower and the difference in fusibility is very marked. With a mixture of fine and coarse material, the fusibility can be so controlled that either the silica mixture or the clay mixture will melt first, according to the proportion of fine material in each. This appears to afford an explanation of some of the contradictory statements made by gas engineers regarding the effect of salt on retorts made of fireclay or silica.

Corrosion is also facilitated by any fine particles in the retort, which offer a more intimate contact between the retort material and the salt. As clays are composed of much finer particles than silica, the reaction will proceed faster with a clay retort than with one of silica; the speed of reaction is also affected by the fact that the compound of the salt with a clay is less fluid than the similar compound with silica. The result is that a retort material containing much grog (which is coarse) may behave in a similar manner, but probably better than one made of silica, whilst a retort whose composition and texture are not known in detail may behave either better or worse than another retort made of apparently the same material. In these circumstances, some engineers will find that retorts high in alumina will give better results than those made of silica, whilst others will have precisely the opposite experience. W. J. Rees states that the corrosion is more severe in ovens built of fireclay than in those built of silica bricks, partly as a result of direct action and partly due to the fireclay bricks shrinking in use and cracking, thus forming open joints which expose a greater area to attack. Silica bricks, on the

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[1] J. W. Cobb has found that common salt volatilises at temperatures below 800° C., and has suggested that the penetration of salt vaporised from the coal into the pores of the retort may be one of the chief causes of corrosion. He also considers that iron compounds present in the coal are converted into chlorides and volatilised with a similar result. If the redeposited iron compound is reduced to the ferrous state it will attack the clay or silica of the retort very readily, forming a powerfully corrosive and fusible silicate.

contrary, tend to expand and so cause serious stresses in the structural work of the oven; suitable natural or artificial mixtures of silica and fireclay produce bricks which neither shrink nor expand and may, therefore, be preferable.

It is *not* the proportion of alumina in the retort which is a decisive factor in the amount of corrosion, but the proportion of real clay (alumino-silicic acid) present, and this is not necessarily proportional to the alumina present, though it will be so in many cases. Hence, comparisons based on the high or low percentage of alumina in a retort may be very misleading. Nor is the refractoriness of the retort material (that is, its temperature of fusion when heated alone) a reliable guide to the action of salts upon it, for the refractoriness, as ordinarily defined, does not take into account the presence of any reacting substance in the contents of the retort.

The destructive action of finely divided carbon in fireclay has been mentioned on pp. 353 and 692. In the case of furnaces, this carbon is often due to the decomposition of carbon monoxide gas, but in retorts it is more likely to be produced by the decomposition of complex hydrocarbon gases which have penetrated into the pores of the bricks. The carbon swells and may bring about the destruction of the bricks.

The effect of slag on retorts is to damage them by (i) abrasion, (ii) penetration (forming holes), and (iii) causing the charge to stick to the retort.

The corrosion will be least when the retort material has a close surface which is not readily penetrated by various salts, and in a porous material it will be least when the grains are coarse and hard-fired, as the hard-firing appears to render them less active (possibly owing to some change in their chemical composition, such as polymerisation). If water can be kept out of the retort, there will be much less opportunity for corrosion to occur, as the presence of moisture seems to be necessary for the decomposition of the salt. If the retorts are made of clay, a large proportion of this should have been burned and made into (coarse) grog before being mixed with the remainder of the clay, so as to keep the proportion of fine particles in the retort as low as possible. In the case of silica retorts, the smallest particles are so much coarser than those of clay that they do not react with the same facility. By using a clay retort made with sufficient grog and burned so as to produce a sufficiently dense surface, it is quite usual to find less corrosion than with a retort made of silica. Hence, the matter of corrosion is primarily one for both the manufacturer and the user: the manufacturer must render all the help he can by making the retort as resistant to corrosion as possible, in accordance with the foregoing suggestions, and the user must do his share by abandoning the use of wet materials or by recognising that, in the presence of moisture, corrosion is almost bound to occur when distilling coal or coke containing an appreciable amount of soluble salts in clay- or silica-retorts.

If entire prevention of corrosion is required, clay and silica retorts are unsuitable and a basic retort material is necessary. This cannot react with the salts and, therefore, cannot be corroded by them. Of the various materials of a basic nature which are applicable, bricks made of sintered magnesite are by far the best; unfortunately, they are very costly, and this will, in many cases, prohibit their use. Moreover, they are peculiarly sensitive to sudden changes in temperature, which is a serious disadvantage in a retort material. The suggestion to line the retort with a magnesia wash is futile, for the magnesia would corrode the retort as much as the salts in the coal. The only washes which appear likely to be suitable are carborundum, chromite, and graphite, all of which are neutral.

In some cases, what is regarded as internal corrosion is really due to rupture under load, and is caused by material adhering to the top and walls of the retort and, later, falling and dragging some of the retort with it.

External corrosion is chiefly due to flue-dust and fuel-ash containing lime, magnesia, iron oxide, potash, and soda, which combine with the clay of the retort, forming fusible slags. This corrosion is best reduced by keeping the dust to a minimum, as when producer gas is used instead of direct firing and by the use of large gas flues, so that very little dust will be carried into the furnace.

The *resistance to abrasion* required in a retort is chiefly with reference to the insertion and removal of the charge. This resistance is sometimes increased by glazing the interior of the retort, but the more usual method is to burn the retort at such a temperature and for such a time that its natural hardness will make it sufficiently resistant to abrasion. Softness is not necessarily a defect in a retort (some retorts which have worked 2000 days are exceedingly soft and porous) and care must be taken not to condemn some retorts merely because they are not as hard as others.

Resistance to abrasion is also secured by using suitably graded material with a suitable bond in such proportions as to give a dense product, yet without spalling. Fireclay bricks are more resistant than silica bricks to abrasion, and clay-bonded silica bricks are more resistant than lime-bonded ones.

The *conductivity for heat* possessed by retorts is of great importance, as the higher the conductivity the smaller will be the amount of fuel required to heat the contents. In a metal retort, the amount of heat which passes through the walls is equal to the specific heat of the material multiplied by the difference in the temperature of the outer and inner surfaces. With retorts made of porous materials, on the contrary, the porosity has a marked effect on the conductivity, and this has led to curiously discordant opinions being expressed as to the relative conductivities of retorts made by different firms or of different materials. The researches of Wologdine, Dougill, Hodsman, and Cobb, and Boyd Dudley are useful in this direction, though they have been made on firebricks and not on retorts.

It is generally correct to say that the greater the porosity of a retort the more likely is it to prove durable under sudden changes in temperature and other conditions of use. But porosity is apparently incompatible with high conductivity, and it is important to learn how a balance may be found whereby the maximum porosity compatible with high thermal conductivity can be obtained. One possible solution may be found in the use of brick retorts, as the bricks can be burned much harder (corresponding to a lower porosity) and yet form retorts which are fully as durable as the softer-burned retorts made in large pieces. As the latter are necessarily porous and so have a low thermal conductivity, they require more fuel to heat them than segmental retorts made of bricks of the same thickness. In opposition to this, however, is the discovery by Dougill, Hodsman, and Cobb[1] that the conductivity of brickwork joints is only about one-tenth as great as that of the bricks themselves, and allowance must be made for this in building retorts.

It is also important to observe that the conductivity values only apply when the heating is constant over prolonged periods, *i.e.* when the materials are in a state of equilibrium. During the period of heating, when the temperature is rising more or less rapidly, the conductivity k must be divided by the product of the specific heat c and the specific gravity s in order to show the extent to which the heat will be diffused through the material. Dougill,

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[1] *Journ. Soc. Chem. Ind.*, 1915, 39, 470.

Hodsman, and Cobb have applied this calculation to their results, but instead of determining the specific heats, they used Heyn and Bauer's figures, with the results shown in the following table :—

TABLE XCV.—HEAT CONDUCTIVITY DURING HEATING (DIFFUSIVITY).

	Heat Conductivity.	Temperature. ° C.	Specific Gravity.	Specific Heat.	Heat Diffusivity.
Fireclay bricks .	0·0028	500	1·95	0·23	0·0062
,, ,, .	0·0040	1000	. .	0·26	0·0079
Silica bricks .	0·0024	500	1·74	0·26	0·0053
,, ,, .	0·0046	1000	. .	0·27	0·0098
Magnesia bricks .	0·0141	500	2·40	0·26	0·0226
,, ,, .	0·0085	1000	. .	0·28	0·0126

It is probable that the rapid heating of silica retorts is due to the greater diffusivity and not to a higher thermal conductivity, as is commonly supposed.[1] Should this be the case, the still greater diffusivity of magnesia should make it more valuable than silica as a material for retorts if its sensitiveness to sudden changes in temperature were not so great as to make it almost impracticable on this account, unless it has been sintered electrically.

The *diffusivity* or rate at which a heat-wave is transmitted through the material is described on p. 375. Strictly, a retort should have a high diffusivity, whilst the rest of the structure should have a low one, so as to prevent undue loss of heat. There is little difference between the diffusivities of silica and fireclay below 1000° C.; above that temperature the diffusivity of silica is slightly greater. Carbide retorts have a much greater diffusivity than those of silica or magnesia, and so have retorts made of clay or silica to which graphite has been added. For further information on thermal conductivity and diffusivity see pp. 194 and 371 to 376.

The *durability* of a retort depends largely on the method of manufacture, the care taken and the conditions to which it is subjected when in use. English gas retorts last, on an average, 700 to 1000 days, but it has been claimed by some German manufacturers that their retorts last 2000 days. Zinc retorts are not very durable owing to the extremely severe conditions to which they are exposed during use. The average life of medium-sized zinc retorts is about 40 days, whilst smaller ones last even shorter periods.

Recent Improvements.—Apart from improvements in the design of retorts used for various purposes, but particularly for gas manufacture, the following improvements have been made since the previous edition of this volume was published :—

(i) Methods of purifying the fireclay have been developed; a considerable amount of injurious material can be rejected by forming a slip of the clay, allowing coarse particles to settle and using the slip after further settling to allow any excess of water to be removed. The use of electrolytes improves the purification.

(ii) The grog and fireclay are much better graded than formerly.

(iii) A larger proportion of grog is now used.

(iv) The proportioning of the various materials is more accurate, and they are much more thoroughly mixed.

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[1] The statement that silica has a thermal conductivity at least 10 per cent. greater than that of fireclay is based on general observation rather than on accurate measurement.

(v) Much better control of the drying is secured in some works, and the period required for drying has been greatly shortened.

(vi) The retorts are now burned at a higher temperature and the last stage of heating is more prolonged, with the result that excessive shrinkage in use is now rare.

(vii) Retorts are now regularly made which conform to a standard specification, so that users can rely more than formerly on obtaining retorts of the quality they require.

(viii) Improvements in the refractory materials have also greatly reduced the cost of the repair and maintenance of coal-carbonising plants, and have increased the productive capacity more than could be foreseen twenty years ago.

Storage.—Retorts, and bricks or blocks for making retorts, should be stored in a dry and preferably warm place, where they will not be exposed to the weather.

They should be handled with care and not " dropped " into position or " bumped " during transport.

Retort Accessories.

The principal refractory accessories for retorts are covers, condensers, and adapters, by means of which the retorts are connected to the condensers. Such accessories when made of refractory material are largely confined to zinc retorts, as the appliances used for gas manufacture are more conveniently made of metal.

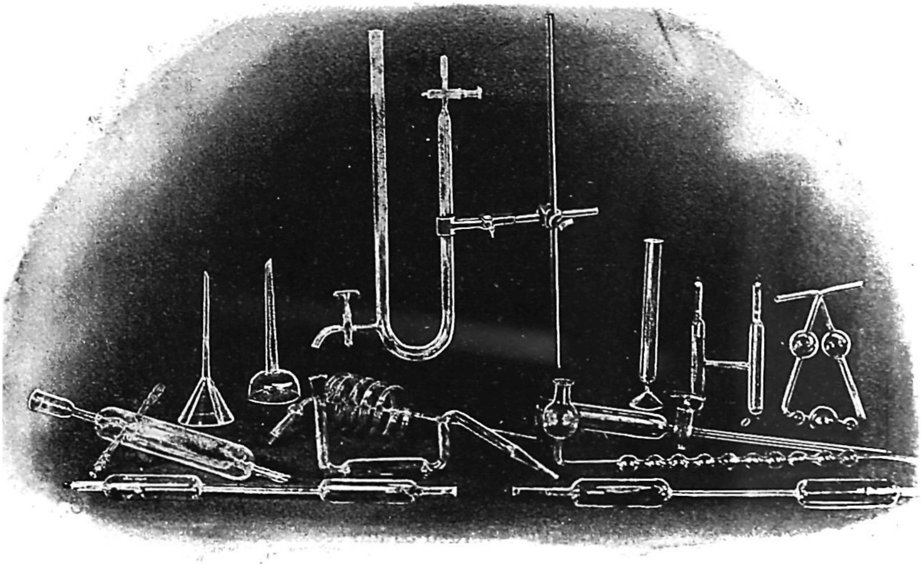
Adapters for zinc retorts are generally made of fireclay, as they are required to resist a fairly high temperature and also a certain amount of corrosion by metallic fumes and molten metal. Iron adapters and connecting pipes should not be used for zinc, as they are too readily oxidised by the gases from the retort passing through them.

Condensers for zinc retorts may be made of much less refractory materials than the retorts themselves, but they must be sufficiently resistant to corrosion to prevent their being damaged by the condensing fumes and the molten metal. They are made of fireclay, to which a large proportion of grog is usually added. They are usually made by the hand-moulding process in the same manner as crucibles for steel, or they may be machine-pressed. After moulding, the condensers are dried for two to three days and fired at about Cone 05*a* (1000° C.), a higher firing temperature being regarded as unnecessary.

CHAPTER XV.

FUSED SILICA WARE.

AMONG the more recently used refractory materials, fused silica has attained great importance in chemical industry, in the laboratory, and, further, is now largely used for domestic and artistic purposes. The development of the manufacture of articles of fused silica or quartz has engaged the attention of many experimental workers owing to the remarkable properties possessed by the material and the possibility of utilising it for scientific and technical purposes, including those for which only platinum or similar costly materials have hitherto been available.



(*By courtesy of the Thermal Syndicate, Ltd., Wallsend-on-Tyne.*)

FIG. 160.—Fused silica ware.

The material is known under various names, of which the most important are *fused silica ware, fused quartz, silica glass, vitreous silica,* and *quartz glass.* This material is produced in three forms—

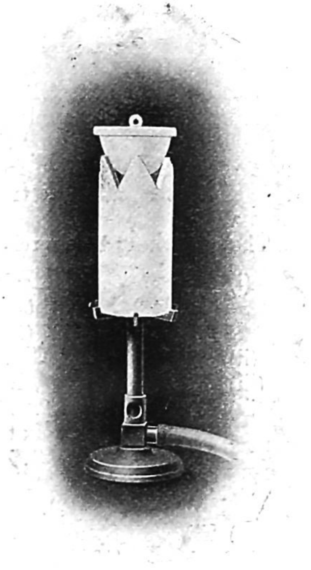
(i) An opaque material.
(ii) A translucent or semi-transparent glass.
(iii) A transparent glass.

The chief advantage of fused silica ware is that its change in volume when heated and cooled is so small that the ware may be subjected to great and sudden changes in temperature without any harmful effect. It is also much superior to glass in its resistance to the action of chemicals, and in its great refractoriness.

Although C. V. Boys, in 1887, had produced fine threads of fused quartz, and Shenstone, Heraeus, and Moissan had independently produced very small articles of fused silica by means of the oxy-hydrogen blowpipe, and whilst small articles of transparent fused silica ware were exhibited by Herschkowitsch in 1900, it was Hutton, Bottomley, and Paget who, in 1904, really placed the manufacture of fused silica articles on an industrial basis, these early articles being of fused silica in the opaque and translucent forms referred to above. Since that date, the further work of Bottomley and Paget, in particular, has done most to bring the industry to its present state of perfection. The Thermal Syndicate, which owns Bottomley and Paget's patents, was started in 1905, while the Silica Syndicate, which developed Shenstone and Kent's patents for the production of transparent quartz glass, and was started in 1907, became allied with the Thermal Syndicate in 1918.

Uses.—The chief use of fused silica as a refractory material is for the manufacture of rods, tubes, plates, crucibles, muffles, retorts, evaporating dishes, combustion tubes, ignition trays, flasks, etc., particularly where corrosive acids are used at high temperatures.

In the chemical industry, it has been used with much success to replace iron and lead in works engaged in the manufacture of sulphuric, hydrochloric, nitric, phosphoric, and other acids, in Glover towers, siphons, condensers, and for evaporating pans arranged in cascades. According to A. Pohl, the use of fused silica ware reduces the cost of manufacture of sulphuric acid on account of the lower fuel consumption and maintenance costs, whilst a better quality of acid is produced with a smaller loss of acid by volatilisation. Fused silica is also very largely used for the manufacture of illuminating gas, and for chimneys and globes for paraffin and incandescent gas lamps. As an electric insulator it is very valuable, especially at high temperatures, so that it is used in the construction of thermo-electric pyrometers, thermostats, and those electric furnaces and radiators which consist of a non-conducting portion with a wire wrapped round it through which the current flows. At temperatures above 1000° C. it should be kept out of direct contact with the resistance wire, which acts as the heating medium.



(Thermal Syndicate, Ltd., Wallsend-on-Tyne.)

Fig. 161.—Fused silica furnace and crucible.

In chemical laboratories, fused silica ware largely replaces Jena laboratory glass and chemical porcelain, and also platinum, where the latter is used as a refractory material.

Fused quartz, in the form of small fragments, may be used in the production of saggars and other articles which are required to resist sudden changes of temperature.

Transparent quartz glass is used for mercury vapour lamps, which require a material specially transparent to ultra-violet rays.

Preparation.—There are two methods in use on a commercial scale for the manufacture of articles of fused silica.

(*a*) The fusion may be effected by means of an oxy-hydrogen blowpipe and, when pure rock-crystal (quartz) is used, this produces a clear, glassy product. The difficulties of manipulation are such, however, that only small articles can be produced.

(*b*) By means of an electric furnace and using a pure sand, it is possible to manufacture large articles, such as vessels of 15 gallons capacity or pipes 12 inches diameter and 30 inches long. This is one of the processes used by the Thermal Syndicate, Ltd. The articles are not transparent like the product from rock-crystals, on account of the minute air-bubbles imprisoned in them, but this does not affect their usefulness for most purposes. The bubbles are, however, a source of trouble where the ware is subjected to abrasion, on account of small cavities formed by the bubbles. The transparent silica ware made of fused rock-crystal is free from this defect. The semi-opaque ware may be made smoother and more transparent by a process of superfusion, which produces a glazed surface.

The following patents relate to the manufacture of fused silica ware :—

(i) Those of the Deutsche Quarz-gesellschaft (including Voelker and Bolle) Ger. Pats. 204,537 (1906), 204,853 (1907), 204,854 (1907), 206,545 (1907), 224,917 (1909), 235,271 (1910) ; Brit. Pat. 5764 (1907).
(ii) W. C. Heraeus, Ger. Pats. 172,466 (1904), 175,385 (1904).
(iii) W. A. Shenstone, Brit. Pat. 4031 (1903).
(iv) W. Vogel, Ger. Pat. 209,421 (1907) ; O. Vogel and Glasfabrik, Dr. M. Schweig, Ger. Pat. 246,179 (1909) ; O. Vogel, French Pat. 411,437 (1910), U.S. Pat. 1,040,818 (1910).
(v) F. Wolf-Burckhardt, French Pats. 432,786 (1911), 438,257 (1911), 453,517 (1913).
(vi) Thermal Syndicate, including H. A. Kent, Eng. Pats. 23,492 (1903), 10,930 (1910), 24,482 (1911) ; J. F. Bottomley, R. S. Hutton, and A. Paget, Eng. Pat. 10,670 (1904) ; J. F. Bottomley and A. Paget, Eng. Pats. 18,437 (1904), 9522 (1905).
(vii) Elihu Thomson (U.S. Patents).

Semi-opaque silica ware is made of the purest silica sand obtainable, because rock-crystal is too costly and the necessity of grinding it to powder adds to the cost. For transparent quartz glass, on the contrary, the crystals must be used, and that is one reason why this form of quartz glass is so costly. The sand should be washed, dried, and sifted, so that the particles may be as clear and uniform in size as possible. The furnace described in Bottomley, Hutton, and Paget's patents serves both for melting the sand and for fashioning the product. It consists (figs. 162 and 163) of a horizontal resistance bar (*a*) of graphite, 24 to 60 inches long and ¾ to 1½ inches diameter. The mould (*f*) is provided with a grid (*g*), through which the unfused sand falls away in order to make room for the glass as it expands under the influence of the air and gradually assumes the shape of the mould. The mould is omitted when not required.

In working a furnace such as that shown in figs. 162 and 163, the current is started in the empty furnace and sand is fed slowly and uniformly. The potential of the current may be low—about 30 to 40 volts—but the current varies from 300 amperes at first, rising gradually to 1500 amperes. When a temperature of 1400° C. is reached, the hydrogen and carbon monoxide reduce the silica to silicon, which, being volatile at 1600° C., permeates the cooler sand grains and "condenses" as it becomes reoxidised. At 1650° C. the sand softens, the grains nearest the resister adhere, the resister itself becoming superficially glazed. At 1750° C. the siliceous mass becomes compact and pasty, and a considerable quantity of carbon monoxide is produced by the reaction of the silica with the carbon resister; this gas exerts a pressure on the silica and separates it completely from the resister; the continued heating of the silica then takes place solely by radiation from the resister. It is important to secure the separation of the silica "collar" from the resister at this stage so as to prevent the silica from being spoiled by spots of silicon carbide, etc. The heating is continued until the meter has registered a total current consumption (usually about 1500 K.w.h. per ton of silica) which has previously been found to be sufficient. The usual time required is 30 to 45 minutes to reach the fusion temperature, and a further 30 to 45 minutes for the fusion itself. At each charge, only about one-third of the contents of the furnace is fused; the remainder constitutes an important loss, as it is permeated with impurities from the fused material and, therefore, cannot be used over again; if so used, it produces fused quartz of very poor quality. Very accurate regulation of the furnace is necessary, as the temperature required to melt the silica is very near that at which it reacts with carbon, and such a reaction must be avoided.

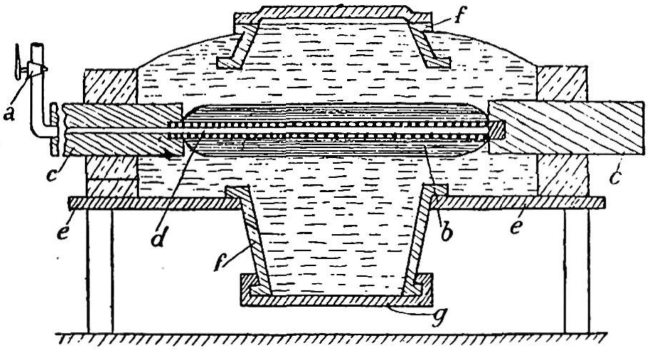


FIG. 162.—Bottomley electric furnace.

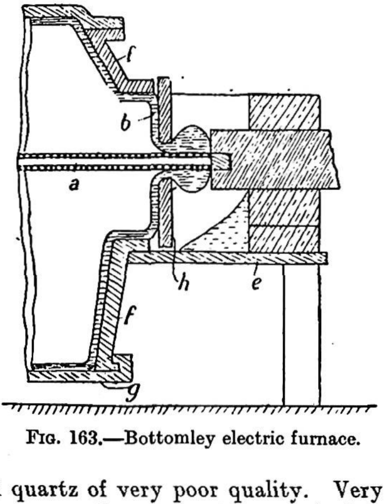


FIG. 163.—Bottomley electric furnace.

W. A. Shenstone[1] found that when fragments of quartz at a temperature of 1000° C. are thrown into water, a white enamel-like product is formed which

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[1] *Proc. Roy. Inst.*, 1901, 525.

may be fused into rods and made into tubes, etc. It is more transparent to ultra-violet rays than ordinary glass; its other properties are those of fused quartz.

For the manufacture of transparent fused silica ware, the purest rock-crystal [1] must be used, as even 0·3 per cent. of impurities will cause opacity. The crystals are heated to redness, plunged into water and ground fine. The powder may be still further purified by washing and treatment with acids if desired. It is made by fusing the powdered crystals in the oxy-hydrogen flame (Heraeus) and by heating directly in an electric arc (Hutton), or in a carborundum crucible heated electrically (Bredel), or in a graphite crucible lined with tungsten (Keyes).

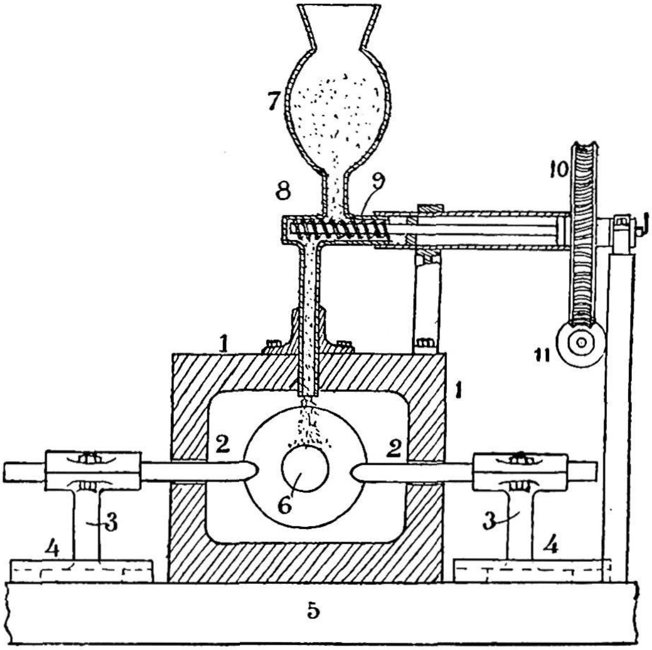

FIG. 164.—Electric furnace of the Thermal Syndicate.

The method used by the Thermal Syndicate (fig. 164) consists in allowing a well-regulated stream of quartz-dust to fall on a small tube of fused silica, which is rotated and subjected to the action of an electric arc or oxy-hydrogen blowpipe in such a manner that the flour is fused almost simultaneously.

The chief difficulty in the manufacture of transparent silica ware is the avoidance of tiny bubbles of gas or air which, when once formed, cannot be completely eliminated, because silica glass is so highly viscous, even at a temperature of about 2000° C., that it cannot be "fined" or made clear by prolonged heating. It is, in fact, so "pasty" that bubbles of gas will not rise in it, nor will small particles of other material separate by sedimentation. The number of air-bubbles may be slightly reduced by repeatedly reheating the material to a high temperature, but this does not remove them completely.

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[1] The Zirkongesellschaft claims that the use of geyserite is superior.

Most of these bubbles can be eliminated by the application of a vacuum; the remainder are made smaller by applying pressure to the soft mass.

Another difficulty is the transformation of α into β quartz at 575° C., which causes the articles to break unless extreme care is taken. Herschkowitsch overcame both these difficulties by heating the crystals so slowly to 600° C. that they undergo complete inversion into β-quartz without cracking, and then melting them as rapidly as possible. If they cool prior to fusion, they will crack and show bubbles or imperfect transparency.

Ware of transparent quartz is wholly fashioned by the oxy-gas blowpipe, an oxy-acetylene flame being usually employed.

Shaping.—Articles of fused silica may be blown or drawn in a similar manner to those of glass, but their production is more difficult on account of the much greater viscosity of the quartz and the very high temperature at which it must be maintained. It was not originally found practicable to mould fused quartz in open moulds in the ordinary manner; the mould was, therefore, made a part of the furnace (fig. 162), in which the fusion occurs. For instance, in the Thermal Syndicate process, the fused sand forms a pasty collar or tube surrounding the central resistance core, and this collar can be either expanded into any desired shape up to 3 feet diameter by compressed air in a mould forming the casing of the furnace, or it may be drawn out by grips and so made into long tubes of any desired diameter and up to 100 feet in length. Worm-coils of 2-inch bore and up to 60 feet in length can be made all in one piece.

The essential feature of Bottomley, Hutton, and Paget's success is the discovery that a great initial pressure of air is required, but that immediately the mass of fused silica begins to expand under the influence of this pressure the remainder of the "blowing" is as easy as that of common glass. The same remark applies to drawing the silica into tubes. A mass of fused silica about 2 feet long and weighing 10 lbs. requires a pull of 55 lbs. at first, but as soon as the mass begins to yield a pull of only 26 lbs. will suffice to draw it to a length of 30 feet. A freshly drawn tube retains its plasticity long enough to enable it to be wound into a spiral figure. A press may be used for some articles, whilst others may be made like those of glass. The interior of tubes, etc., made of quartz glass is smooth and shiny, but the exterior is usually roughened by grains of imperfectly fused sand. These may be removed by a sand-blast. Articles of fused silica are cut to shape, when necessary, by means of carborundum or emery wheels, or by the ordinary lapidary's cutter. They are polished on wheels fed with wet sand, precisely like ordinary glass.

The opacity of quartz glass may be reduced by treating the crudely polished surface with hydrofluoric acid, or by surrounding the mass of fused silica in the furnace with a carbon tube which, on continuing to heat the silica, produces a glossy surface similar to that produced by the resister. A greater transparency can also be given by re-fusing the surface of the ware by means of an oxy-hydrogen blowpipe or an electric arc.

Properties.—The following properties of vessels, tubes, etc., made of fused silica are of interest; they refer more particularly to the products of the Thermal Syndicate, Ltd., which are sold under the trade name of "Vitreosil," but are largely applicable to all ware made of fused silica. The principal properties of fused silica which render it of such value to the chemical and allied industries are its great resistance to sudden changes of temperature and to acids.

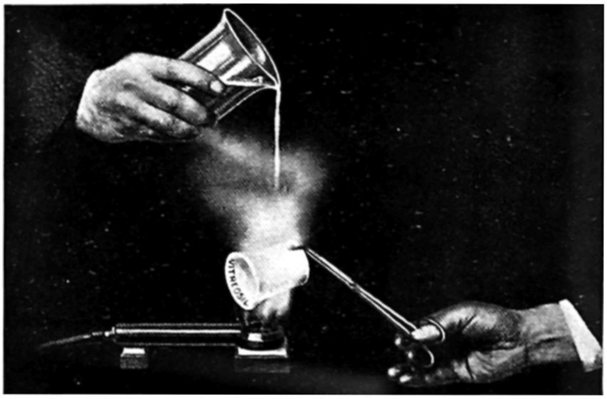
Resistance to Heat.—Fused silica is amongst the most refractory of materials, melting at about the same temperature as platinum (between 1700° C. and

PROPERTIES

1800° C.). The melting-point is, however, not well defined, as an appreciable softening of the material takes place at about 1500° C., especially if under pressure, or if the article is supported only near its ends. The temperature employed must not be too high, for, as explained below under " Devitrification," articles made of fused silica which are repeatedly heated to 1200° C., shrink irregularly and gradually break up or devitrify on account of the gradual change from the glassy to the crystalline (cristobalite) state, with a contraction of about 5 per cent. The disintegration occurs much more rapidly in the presence of dust of an alkaline or basic nature, such as the ash from fuel.

For information on the thermal conductivity of quartz glass see p. 710.

The *volatility* of silica at about 1600° C. is considerable, particularly in the presence of hydrogen or carbon monoxide; these first reduce the silica to silicon, which is readily volatile and is reoxidised in the furnace. Wartenburg has shown that silica is reduced to silicon at 1300° C. to 1400° C. by hydrogen, and by carbon at 1250° C. The vapour-pressure curve of silica rises very steeply from 65 mm. at 1890° C. to 760 mm. at about 2100° C., and the loss of material when working at these high temperatures is considerable.



(Thermal Syndicate, Ltd., Wallsend-on-Tyne.)

FIG. 165.—Insensitiveness of a fused silica vessel.

Insensitiveness to Temperature Changes.—Articles made of fused silica are remarkably insensitive to sudden changes in temperature. Thus, a cold tray made of this material may be placed at once into a red-hot muffle without damage, and various parts of a tube may be maintained at widely different temperatures. This insensibility makes fused silica particularly valuable for pyrometer sheaths and for many industrial and chemical purposes. In the case of small muffles, this insensitiveness, combined with high impermeability to gases, is very valuable. It is also a fact that small articles can be made red-hot and plunged into cold water without cracking. This remarkable property is due to the extremely small coefficient of expansion of fused silica, the average figure for temperatures below 1100° C. being ·00000059, which is about one-eleventh that of glass and about one-twenty-fourth that of rock-crystal. Quartz glass also has the advantage of expanding perfectly regularly up to 1000° C., whereas the expansion of ordinary glass is irregular. The following table shows the coefficient of expansion at various temperatures :—

TABLE XCVI.—EXPANSION OF FUSED SILICA.

Temperature ° C.	Coefficient of Linear Expansion.	Authority.
−191° to 16°	0·000000256	F. Henning.
16° „ 250°	0·000000539	„
16° „ 1000°	0·000000540	„
200°	0·000000518	Randall.
500°	0·000000568	„
900°	0·000000538	„
1100°	0·000000583	„
0° to 1000°	0·000000700	Le Chatelier.

More recently, Holborn and Henning have found the expansion between 0’ C. and 1000° C. to be strictly proportional to the rise in temperature, and obtained as an average figure 54×10^{-8}, whilst glass is $600 - 900 \times 10^{-8}$. The shrinkage of about 5 per cent. observed when fused quartz reverts to cristobalite explains the spontaneous disintegration of this material when subjected to prolonged heating at 1500° C. or above.

For further information on the thermal expansion of fused silica see Rigby and Green, *Trans. Cer. Soc.*, 1938, **37**, 367.

Fused silica is practically free from thermal hysteresis and so retains its original volume almost perfectly after prolonged or repeated heating and cooling.

Devitrification.—Fused silica ware appears to be amorphous—like glass—but it may consist of extremely minute crystals of cristobalite; this may be inferred from the X-ray spectrum and the calculated distribution of the particles.[1] It may, also, be amorphous in the sense that no unit of structure repeats itself regularly in three dimensions, but forms a " random " network.

When fused silica ware is maintained at a temperature of 1200° to 1600° C. for a considerable time and then cooled it *devitrifies*, *i.e.* it becomes obviously crystalline, though the total proportion of the obvious crystals seldom exceeds 5 per cent. with a transparent fused quartz of good quality.

The devitrification is seldom apparent at temperatures above 230° C., *i.e.* above the reversion point of α into β cristobalite. At this point, the cristobalite contracts about 5 per cent., and the tiny cracks so produced act as nuclei and facilitate the crystallisation. Repeated heating for a short time has the same effect as a single, prolonged heating. The best method of avoiding the trouble due to devitrification is not to allow the quartz glass ever to cool below 300° C.; this is a very difficult restriction to its use.

The National Physical Laboratory has reported as follows:—

" In general, the loss of strength hardly commenced at 1120° C.; at 1188° C. it existed, but was not very serious, even after eight hours' heating; but four hours' heating at 1350° C. produced a reduction of 40 per cent. to 50 per cent. in the strength, showing that the rate of loss of strength increases very rapidly as the temperature rises."

It will, therefore, be seen that although fused silica cannot be exposed continuously to temperatures exceeding 1200° C., yet if the heating is not continued for long periods, the material may be used successfully for much

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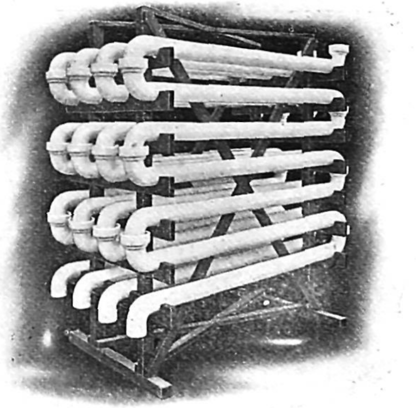
[1] Randall, Rooksby, and Cooper, *J. Soc. Glass Tech.*, 1930, **14**, 210; Zachariasen, *J. Amer. Chem. Soc.*, 1932, **54**, 3841; Warren, *J. Amer. Cer. Soc.*, 1938, **21**, 49.

higher temperatures. For example, in pyrometric measurements, tubes made of fused silica are largely used for rapid readings at very high temperatures.

The risk of devitrification is also reduced if silica ware is not heated from cold too often; *i.e.* it is better to keep a silica muffle at a temperature above 250° C. when not in use rather than to let it cool completely.

The *chemical properties* of quartz glass are almost exactly the same as those of quartz and of other forms of silica.

Solubility.—Silica glass is quite insoluble in boiling water, and in most acids, alkalies, and other solutions; it finds, *inter alia*, a use as boiler gauge glass, where its life is much longer than any glass which may be used for this purpose. Kohlrausch has found that water distilled in fused silica ware has a conductivity of only $0{\cdot}72 \times 10^{-6}$ mho per cubic centimetre. Consequently, vessels of quartz glass are far superior to those of resistance glass for analytical work of great precision.



(*Thermal Syndicate, Ltd., Wallsend-on-Tyne.*)

FIG. 166.—Fused silica cooler.

Resistance to Acids.—Fused silica is unaffected by acids, with the exception of hydrofluoric acid and, at high temperatures, phosphoric acid. The action of phosphoric acid on silica is slight, and commences above 300° C., so that for all ordinary purposes fused silica can be safely used with this acid.

Gautier and Clausmann have found that the solubility of ordinary glass in hydrofluoric acid as compared with silica glass is as 10 : 1.

Sulphuric, nitric, and hydrochloric acids, or a mixture of them, such as aqua regia, have absolutely no action on the material.

Except for heating hydrofluoric acid and phosphoric acids, platinum vessels may be satisfactorily replaced by those of fused silica, which is not only much less expensive, but less liable to damage from possible splashings of oxides.

Resistance to Alkalies.—Quartz glass is soluble in hot solutions of alkaline hydrates and carbonates, though the actual amount dissolved is so small as to be usually negligible. The results by Mylius and Meusser given in Table XCVII. show the weight of quartz glass dissolved from an exposed surface 90 square centimetres (14 square inches) in area.

Fused silica is sufficiently resistant to alkalies for crucibles made of it to be used for the ignition of vegetable matter, coal, etc., which leave a basic or alkaline ash; at the temperature ordinarily reached in such ignitions (about 900° C.) the fused silica is not attacked any more violently than refractory porcelain. At higher temperatures, alkalies and bases combine with the silica, forming fusible silicates.

Silica crucibles cannot be used to replace platinum crucibles where substances containing alkalies and bases are to be heated to a very high temperature, as such materials attack the silica readily.

Resistance to Oxides and Metals.—Copper oxide, lead oxide, and many other metallic oxides and some metals, more particularly calcium, magnesium, aluminium, nickel, sodium, potassium, and cerium, exert a serious corrosive action on silica glass owing to their reducing action on the silica at a red heat. Quartz glass tubes are sometimes attacked by nickel-chrome wire at 900° C. to 1000° C. after prolonged heating in an oxidising atmosphere.

TABLE XCVII.—SOLUBILITY OF QUARTZ GLASS.

Temperature.	Time of Contact.	Reagent.	Concentration.	Loss in Mgms.
18° C.	2 days	Ammonium hydrate	10 per cent.	0·8
		Sodium "	10 "	0·4
		Potassium "	30 "	1·2
18° C.	14 "	Sodium hydrate	1/N	2·0
		" carbonate	1/N	0·6
		Barium hydrate	Saturated sol.	nil
		Sodium phosphate (acid)	" "	nil
100° C.	3 hours	" hydrate	2/N	33·0
		Potassium "	2/N	31·0
		Sodium carbonate	2/N	10·0

Finely crushed silica reacts rapidly with lime at 1000° C., but the reaction with pieces of silica glass, quartz, and cristobalite is much less violent and is seldom serious below 1400° C. Above this temperature, according to Hedvall, bi-calcium silicate, $2CaO.SiO_2$, is formed, but below it, only the monosilicate, $CaO.SiO_2$, is formed, the minimum temperature of formation of the bi-calcium silicate being 1390° C. to 1420° C. when precipitated silica is used, and 1412° C. to 1444° C. when quartz glass, quartz, or cristobalite is employed.

Stains in vessels of fused silica may be removed by fusing a little potassium bisulphate in them.

Optical Properties.—The principal properties of quartz glass are—

Refractive index	1·45848[1]
" power	0·45848
Mean dispersion	0·00675
Dispersive power	0·01472
Reciprocal relative dispersion	67·92

The *mechanical properties* of quartz glass have not been fully examined, but it has long been known that the crushing strength is greatly reduced at temperatures above 1300° C. V. Bodin has found that the crushing strength of fused quartz decreases as the temperature increases up to about 1000° C., after which it increases up to 1300° C. and then decreases somewhat rapidly. At ordinary temperatures, a compressive load of 7 tons per square inch may be safely applied to the opaque material, this giving a high factor of safety. The tensile strength calculated from the breaking of bars of the material is about 400 lbs. per square inch for the translucent material and 4000 lbs. per square inch for the transparent material.

The impact strength[2] is:

Translucent silica	11,750 lbs. per sq. in.
Transparent silica	12,100 lbs. per sq. in.

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[1] The refractive index of other forms of silica is shown on p. 156.

[2] B. Moore, *J. Sci. Inst.*, 1935, **12**, 108.

The modulus of rupture is:

	Transverse.	Torsion.
Transparent silica . . .	9200	6750 lbs. per sq. in.
Translucent silica . . .	4000	2300 lbs. per sq. in.

The modulus of elasticity (Young's) varies with the temperature. For transparent fibres and rods it is:

Temperature, 0° C.	lbs. per sq. in.
0	$9{\cdot}7\times10^{3}$
300	$10{\cdot}0\times10^{3}$
700	$10{\cdot}4\times10^{3}$

The modulus of elasticity of various forms of silica is based on its increase in length relative to the tension applied to it. Expressed in kg. per square mm., it varies with the form of silica as follows:—

TABLE XCVIII.—MODULUS OF ELASTICITY OF SILICA GLASS, ETC.

Material.	Modulus of Elasticity. Kg. per Sq. mm.	Authority.
Opal	3·890	Auerbach.
Quartz glass	6·970	,,
,, ,, ...	6·240	Schulze.
,, (perpendicular to axis) . .	8·560	Auerbach.
,, (parallel to axis) . . .	10·620	,,
Jena glass	4·500	Schott.
	7·500	,,

The *elasticity* of quartz glass is sufficiently high to enable galvanometer threads of great fineness to be produced from it very satisfactorily.

The *hardness* of fused silica ware is not so great as is sometimes supposed, and mortars made of this material are not so satisfactory as those made from agate or porcelain, as they are not so hard as either of these materials, and are not even so hard as some glasses.

The hardness of quartz glass expressed in kg. per square mm. (Hertz and Auerbach) and on Mohs' scale is as follows:—

TABLE XCIX.—HARDNESS OF SILICA, ETC.

Material.	Absolute Hardness. Kg. per Sq. mm.	Mohs' Scale.
Quartz glass . .	223	5
Common glass . .	130-265	4-6

Electrical Properties.—As an electrical insulator, fused silica is superior to glass and porcelain. The resistance decreases very slowly with a rise in temperature. It also possesses the further advantage that moisture does not condense on its surface, and, in consequence, the surface leakage is much smaller than is the case with glass and materials of a ceramic nature.

Table C., from a report by the National Physical Laboratory, and Table CI., from the American National Advisory Committee's Aeronautics Report, give a comparison of the insulating properties of fused silica and certain glasses, porcelains, etc., at various temperatures.

TABLE C.—COMPARISON OF INSULATING PROPERTIES OF FUSED SILICA AND GLASS.

Fused Silica.		Glass (Soda-Lime).		Glass (Jena Combustion Tubing).	
Temperature. ° C.	Resistivity Megohm-cm.	Temperature. ° C.	Resistivity Megohm-cm.	Temperature. ° C.	Resistivity Megohm-cm.
15	Over 200,000,000	18	500,000	16	Over 200,000,000
150	„ 200,000,000	145	100	115	„ 36,000,000
230	„ 20,000,000	..	..	150	„ 18,000,000
250	„ 2,500,000	..	..	750	0·1 to 0·4
350	„ 30,000	..	..	..	..
450	„ 800	..	..	..	..
800	About 20	..	..	..	..

The specific inductive capacity is 3·5 to 3·6.

Tests were also made on the di-electric strength, but with the pressures which were available, the breaking-down point could not be determined. The voltage employed was 30,000, and the thickness of the material 1·2 mm.

TABLE CI.—COMPARISON OF INSULATING PROPERTIES OF FUSED SILICA AND PORCELAIN.

	Resistivity at 500° C. Megohms-cm.^{3}.	Temperature at which Resistivity – 1 Megohm-cm.^{3}.
Fused silica	340	890° C.
Best porcelain tested	80	790° C.
Mica plug insulator	70	720° C.
Porcelain plug insulator (Aviation work)	40	650° C.
„ „ „ (average automobile work)	0·80	490° C.

The *specific inductive capacity* is 3·7 to 4·2.

The *breakdown* (*puncture*) *values* are approximately:

	Temperature. ° C.	Thickness.	KV./mm.
Translucent silica . . .	10–25	+5 mm.	10
	500	+5 mm.	2–3
Transparent silica . . .	10–25	+2 mm.	20
	500	+2 mm.	3–5

The dielectric properties, high breakdown value (over 10 KV. per mm. at ordinary temperature) and low power factor (0·1 per cent.) also show that vitreous silica is one of the best insulating materials, especially at high frequencies. It is much superior to porcelain.

The *electrical conductivity* of silica glass, according to Pirani and Siemens, is $0{\cdot}25 \times 10^{-4}$, this value being the reciprocal of the resistance of a cube of 1 cm. side at 727° C. Recent measurements seem to show that this result may be too high.

The *specific gravity* of clear fused silica ware is about 2·2; that of the opaque variety is 2·08. The specific gravity of fused quartz varies with the uniformity or homogeneity of the material. The vitreous silica retains so many minute air-bubbles that it has an apparent specific gravity between 2·07 and 2·15, whilst the transparent, well-fused quartz has a true specific gravity of 2·20.

The *specific heats* of quartz, cristobalite, and quartz glass tend to coincide at high temperatures, and also to increase as the temperature is raised, as shown in Table CII., which is based on determinations by W. P. White.

TABLE CII.—SPECIFIC HEAT OF SILICA.

Temperature.	Quartz Glass.	α-Quartz.	β-Quartz.	Cristobalite.
100° C.	0·202	0·204	..	..
250° C.	0·236	0·244	..	..
500° C.	0·266	0·294	..	..
550° C.	..	0·313	..	..
750° C.	0·280	..	0·277	0·278
1000° C.	0·290	..	0·288	0·285
1100° C.	..	..	..	0·287

The specific heat of quartz glass is affected by devitrification at the higher temperatures in the table.

The *thermal conductivity*[1] of opaque silica ware is similar to that of glass, 0·0025 cal./sec./cm./cm.^{2}/° C.; that of transparent silica is 0·0035 unit.

The *latent heat of fusion* of silica has not been determined directly, as the experimental difficulties are too great. According to Richards' and Vogt's formulæ respectively, it should be 65 cal. per gramme.

Permeability.—Articles made of fused silica are permeable to some gases at high temperatures. Hydrogen and helium diffuse through it above 330° C. and at a pressure below that of the atmosphere, while nitrogen and oxygen only diffuse at atmospheric pressure at a temperature above 430° C. The permeability increases with the temperature and pressure. Wästner has shown that the permeability of silica glass follows the general laws of diffusion of gases. At temperatures between 700° C. and 1000° C., the absorption of hydrogen in fused silica is of the same order of magnitude as that of hydrogen in water at ordinary temperatures. This permeability is a serious drawback in the case of pyrometer tubes made of silica and containing platinum wires, but the impermeability at lower temperatures makes the ware of great value for many purposes. More recent measurements by Johnson and Burt[2] up to 1000° C. with hydrogen, nitrogen, and argon do not show that the permeability follows the general laws of diffusion, the rate of entry of gas into an evacuated vessel

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[1] Communication from the Thermal Syndicate, Ltd.

[2] *J.O.S.A. and R.S.I.*, vi. 7, 22.

varying as the third or higher power of the temperature. The transfusion is, however, slight even at elevated temperatures, and does not prohibit the use of silica as a gas-tight envelope for high-power thermionic valves, for which purpose it has numerous advantages.

ZIRCONIA-QUARTZ OR SILOXIDE WARE.

F. Wolf-Burckhardt and A. Borchers (French Pat. 432,786) in 1911 produced a quartz glass, for which they claimed a greater fusibility, but higher temperature of vaporisation by adding 1 to 5 per cent. of titanium oxide or zirconia to the sand used for making the quartz glass. They stated that oxides of aluminium, cerium, chromium, tungsten, uranium, and vanadium may be used in a similar manner. These complex glasses were termed siloxides by Thomas, who stated that whilst they may be used for most of the purposes for which pure fused silica is used, they are much more easily made, refined, and shaped; but the investigation of these glasses is still incomplete. The patentees claim that the addition of 1 per cent. of zirconia (p. 239) to fused silica makes it more resistant to alkalies, reduces its tendency to devitrify, and increases its mechanical strength. On the other hand, the objection has been raised that this claim is not correct, and that any addition of titania, zirconia, etc., to silica increases the tendency to devitrify.

CHAPTER XVI.

REFRACTORY PORCELAIN.

UNDER the term " refractory porcelain " is included all porcelain ware made to resist the combined action of heat and acids, such as the evaporating basins, tubes, etc., used in chemical manufacturers' laboratories and the ware for pyrometers and other scientific instruments. Great progress has been made in the manufacture of refractory ware during the past two decades, one of the results of which has been that French refractory porcelain has been largely replaced by the German ware. Indeed, in Germany, the manufacture has been so successful and the prices so reasonable, that the production of this ware was, for some years, almost exclusively confined to that country.

The essential constitution of a true porcelain is that of a felted mass of refractory crystals (usually mullite) embedded in a glassy matrix of previously fused material. The materials used may be varied to produce porcelains with certain distinctive qualities, so that whilst the base in ordinary porcelain is potash or soda, in some of the refractory ones the base is magnesia.

Many of the so-called " refractory porcelains " are not true porcelains, but are vitrified clays or fused metallic oxides. Hence, commercially, the term " refractory porcelain " includes—

(i) *True porcelains*, composed of clay, felspar, and free silica.

(ii) *Clays* which have been heated to a state of vitrification.

(iii) *Metallic oxides*, such as magnesia, alumina, and zirconia, which have been heated to vitrification or incipient fusion. These have been described in Chapters I., V., and VIII., but their value in replacing the true porcelains as a refractory material is not so fully appreciated as it deserves to be.

The chief properties of these sintered oxides are:

Sintered alumina consists largely of recrystallised α-corundum crystals with a fusion-point of 1800° C.; it resists hydrogen up to 1870° C. Hardness=9.

Sintered spinel has a melting-point of 2135° C. It has a very low heat-conductivity and, therefore, a high insulation power and a high resistance to alkalies and bases.

Sintered beryllia has a melting-point of 2550° C. It is more basic than sintered alumina and is more subject to attack by acids. In contact with carbon it is reduced at 2000° C. It is very insensitive to thermal shock. It forms fusible slags with some oxides.

Sintered zirconia has a fusion-point of 2680° C. It is used for melting metals, also slags and some glasses. It is very sensitive to thermal shock and has a low thermal and high electrical conductivity.

Sintered zircon can be used up to 1750° C. It is very resistant to acids, but not to alkalies. It is used in some high-frequency furnaces.

Sintered magnesia has a melting-point of 2750° C. It is very resistant to basic materials. It is used for melting refractory metals.

(iv) Mixtures of clays and metallic oxides forming ware more or less like the true porcelains included under (i).

True Porcelains.—Ordinary European hard-paste porcelain is usually made of—

Clay	50 parts
Felspar	25 „
Quartz	25 „

but many variations from these proportions exist. Of the three ingredients used, the clay is the most refractory, the quartz serves to reduce shrinkage, and the felspar acts as a flux and thus forms a vitrified mass. Under some conditions, the quartz also acts as a flux. To increase the refractoriness of such porcelains, it is necessary to replace the quartz by a more refractory material, alumina being eminently suitable, inasmuch as it is refractory, non-shrinking, and capable of being finely ground. Unfortunately, pure alumina is too costly, and the various forms of less pure alumina (corundum, thermit waste, etc.) are too impure for use in refractory chemical ware. In all cases, the alumina must be burned repeatedly at Seger Cone 18 (1500° C.) or above, or it must be fused electrically in order to make it perfectly constant in volume.

It has been found that porcelains containing less than 15 per cent. of felspar and 40 per cent. of clay are the least sensitive to sudden changes in temperature.

The refractoriness of a true porcelain is at a maximum when the proportion of alumina is high and that of felspar or base is low, the clay also being kept as low as possible consistent with working power. In most instances, the following are the maximum proportions which can be used for ware which has to be thrown, cast, or moulded:—

Best china clay	30 parts
Felspar	25 „
Calcined alumina	45 „

Such a mixture has a fusing-point of Seger Cone 35; it is very slightly attacked by fluxes, but, unfortunately, it begins to soften at a temperature of about Cone 22, or very little above that of ordinary hard porcelain. A more refractory material is obtained by first heating a finely ground mixture of equal parts of felspar and pure alumina repeatedly at Seger Cone 16 and then mixing equal weights of this product, china clay, and highly calcined alumina. The mixture is moulded into the desired shapes and burned at Seger Cone 17 (1480° C.).

Refractory porcelains can also be made from calcined minerals of the sillimanite group (p. 146) and china clay—usually in equal parts. They are highly refractory, very resistant to changes in temperature and of great density, but they require to be burned at about 1650° C.

The hard-paste, *Berlin porcelain*, extensively used for laboratory purposes, such as evaporating dishes, crucibles, tubes, etc., has a composition averaging: Silica, 69·5; alumina, 26·6; iron oxide, 0·8; titanium oxide, 0·4; lime, 1·4; magnesia, 0·3; potash, 0·3; and soda, 0·7 per cent. Its characteristics are described on pp. 717, 720.

Good French recipes for refractory porcelain are—

	A.	B.
Beauvoir kaolin	50	..
St Yrieix kaolin	20	21
English china clay	..	43
Sand	10	16
Felspar	10	16
Chalk or calcite	3	4
Broken porcelain (*pitchers*)	7	..

The second of these materials (B) is known as *Larchevèque's porcelain*; it is extensively used and is regarded as superior to A.

Magnesic porcelains are highly refractory and have been known since 1770, though greatly improved since that time.

Magnesic porcelains are specially valuable on account of their insensitiveness to repeated and sudden changes in temperature, their long range of vitrification, low coefficient of expansion, high thermal conductivity, great mechanical strength, and low porosity.

The following are typical mixtures, the first and second being chiefly of historic interest, whilst the third is made at the State Factory, Berlin:—

TABLE CIII.—MAGNESIC PORCELAINS.

	Giovannetti (1770).	Salvétat.	Heinecke.
Magnesite	28	17	72
Ball clay	9	25	..
Felspar	7	..	..
Quartz	28	54	..
Fragments of porcelain (pitchers)	28	..	..
Marble	..	4	..
Alumina	..	..	28
Molecular ratio $Al_2O_3 : MgO$	5·5	4·4	3·0

Heinecke's mixture is finely ground and repeatedly burned at Seger Cone 17 and, after cooling, is again ground to powder. It is then mixed with dextrin or other suitable agglutinant, made into articles and burned at Cone 32. This is the most refractory of magnesic porcelains, and, being free from silica, it is of special value for investigations in which siliceous vessels must be avoided.

Instead of using the raw magnesite, better results may be obtained by substituting an equivalent amount of finely ground sintered magnesia.

E. T. Montgomery[1] has obtained excellent results in this way with mixtures such as—

	A.	B.	C.	D.
Ball clay	30	30	20	30
Georgia kaolin	20	..	..	55
Fused magnesia	50	70	80	15

He found that mixture D, when burned at Seger Cone 12, yields a product impervious to gases and liquids and highly resistant to sudden changes in temperature.

The great variation in composition is striking, especially as very little difference is observable in the useful properties of the products, all of them

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[1] *Trans. Amer. Cer. Soc.*, 1913, **15**, 606–619.

having a refractoriness greater than Seger Cone 32 and showing great resistance to sudden changes in temperature.

Steatitic porcelain is of the magnesic class, being made of steatite or talc ($3MgO.4SiO_2.H_2O$), a natural magnesium silicate which occurs as scaly aggregates and as compact masses of a white, grey, green, brown, or red colour, and having a specific gravity of 2·7. It is extremely soft, its hardness being only from 1 to 1½, so that it may be readily scratched by the finger-nail. It is, however, highly refractory. Varieties of the same substance are known as *soapstone* and *potstone* on account of their soft and greasy appearance, and sometimes as *French chalk.* The material is crushed to powder and mixed with a small proportion of fireclay or other bond, moulded under great pressure and then burned at a temperature as high as the articles will stand without loss of shape. In J. E. G. Meran's (1893) patent no temperature is specified; the author of the present volume recommends 1400° C. or above, but much depends on the steatite used. The manufacture of refractory articles of *fused steatite* was patented in 1908 by the British Thomson-Houston Co., this patent applying specially to the production of tubes.

The steatite porcelains used for the manufacture of gas-burners, sparking plugs for internal combustion engines, etc., are not wholly magnesic porcelains, but complex mixtures. The composition of these steatite porcelains varies with different makers; one well-known firm uses a mixture made of 50 parts of china clay, 40 parts of felspar, 10 parts of flint, and 6 parts of steatite.

The term *steatite porcelain* is commonly applied to all products containing more than 70 to 90 per cent. of steatite or talc, though it ought, strictly, to be confined to those burned at such a temperature as will produce an almost impervious body composed of a mass of felted crystals surrounded by a glassy matrix. Many " steatite porcelains " contain little or no crystalline matter.

Some of the earlier steatite porcelains had the composition A in Table CIV., but most modern steatite bodies more closely resemble composition B.

TABLE CIV.—STEATITE BODIES.

	A, Old.	B, Modern.	
Talc	70	82–86	per cent.
Ball clay . . .	25	10–13	,,
Flint . . .	5	2–6	,,

A very large number of patents have been granted for steatite bodies, particularly for sparking plugs and electric radiators. Among these, the following are interesting:—

(i) Steatite or talc 80, plastic clay 10, and kaolin 10 parts (Eng. Pat. 410,260—1932).

(ii) Steatite or talc 83, barium carbonate 9, calcium carbonate 5, and clay 3 parts (Eng. Pat. 424,601—1933).

(iii) Soapstone 58, rutile 32, blue clay 6, and calc-spar 4 parts (Eng. Pat. 429,730—1933).

Several patents mentioned in Chapter V. are also interesting to manufacturers of refractory porcelains.

The average composition of the steatite insulators in electric hot plates in the United States is—

Steatite	20–25	per cent.
China clay	80–75	,,

but some firms use a mixture corresponding to Composition B in Table CIV., but with felspar instead of flint.

The toughness of such bodies is attributed to the crystals of magnesium silicate. Their low resistance to thermal shock is due to their expansion (8×10^{-6}), which is greater than that of true porcelain.

Another variety of steatite porcelains consists entirely of steatite, this material being ground to a fine dust and used as a body. If desired, a small proportion of vitrifying material may be added to it, so as to secure the production of a wholly vitreous mass, but this is only necessary in the case of the purer steatites. Felspar and china clay form the basis of the vitrifying materials used for this purpose. This kind of porcelain has been extensively used for the manufacture of insulators; before the War, these were made almost exclusively in Germany, but more than one British firm has since commenced their manufacture with great success, and now produces insulators fully equal to those formerly imported from abroad.

The use of many other mixtures has been patented in various countries, but they are not of sufficient importance to be detailed here.

In some cases, articles may be made by carving the raw steatite or talc to the required shape.

The great advantage of steatite, or talc, in a material of a vitrified nature is that it increases the amount of fused material present without serious risks of loss of shape being run, as is the case when mixtures containing lime compounds are employed. The addition of steatite also increases the toughness of the material, both this property and the lessened risk of distortion being due to the toughness and viscosity of the fused steatite. For some purposes, such as tips for gas-burners, magnesium silicates are an advantage, because they are very insensitive to sudden changes in temperature, and talc or steatite, either alone or mixed with a pottery or porcelain body, is largely used.

It has been found that a mixture of 85 parts of talc and 15 parts of gelatinous precipitated magnesium silicate is particularly good for articles which have to resist sudden changes in temperature, as it possesses sufficient elasticity to be easily pressed to the required shapes without having the disadvantages which accompany the use of clay, especially during drying.

Sinter-corund—a form of sintered alumina (p. 208)—is extensively used for sparking plugs and for other-purposes as a refractory porcelain of high electrical insulating power. The alumina is maintained at a temperature slightly below 1800° C. (which is well below the melting-point of pure alumina) and, on cooling, crystallisation occurs (see Eng. Pat. 415,579—1933). The product has a specific gravity of 3·9, a refractoriness of 2050° C., and a hardness of 9 on Mohs' scale. It is wholly impervious to water, and also to gases below 1720° C. The thermal conductivity is high. The electrical resistivity is 10^{15} ohm-cm. at 800° C., as compared with 10^{10} and 10^{6} for porcelain. Its thermal expansion at 800° C. is 80×10^{-7}. Its resistance to thermal shock is superior to that of porcelain and steatite.

Stoneware mixtures may be used where the colour of the product is not of great importance. The chief difference between stoneware and porcelain is that slightly less pure clays, which are cheaper than china clay, may be used for stoneware; and as these are often more plastic, an easier-working paste is produced. In refractory stoneware, fireclay is often substituted for china clay; in all other respects the materials and mode of manufacture are the same as for refractory porcelain.

Vitrified clays are not quite so satisfactory for refractory work as the true porcelains, though for some purposes they form good substitutes. The clays used for this purpose are usually mixed with calcined alumina, so as to increase their refractoriness. They owe their properties largely to the metallic oxides present in them, which form a sort of porcellaneous matter in the pores of an otherwise refractory skeleton.

Hecht's porcelain is typical of this class of material, which has been found to be specially suitable for pyrometer tubes. It is made by burning a particularly refractory clay (Rakonitz fireclay) with one-sixth of its weight of calcined pure alumina at Cone 20 (1530° C.), grinding this grog extremely fine and mixing it with somewhat less than half its weight of a highly plastic ball clay (Vallender clay being the one actually used). The mixture is burned at Cone 16 (1460° C.), which is about 80° C. below its vitrifying-point. The glaze used for this ware is composed of—

Felspar	6 parts
Marble	8 „
Magnesia	1 part
Halle kaolin	40 parts
Quartz sand	45 „

This glaze is fired on the goods at Seger Cone 16 (1460° C.).

A superior material, very similar to Hecht's porcelain, is widely used for chemical ware under the name of *Marquardt's porcelain.* It is manufactured solely by the State Porcelain Factory in Berlin; the precise composition has never been published, but, from an analysis made by A. J. Phillips in 1913 of an inner and outer Marquardt's pyrometer tube, the materials used correspond to the following:—

	Inner Tube.	Outer Tube.
Calcined alumina	30	40
Burned kaolin or china clay	40	30
Raw ball clay	30	30

The mixture is made into a paste with water; the tubes are formed by extrusion through a die and are burned whilst in a vertical position. W. L. Howart has suggested that tubes should be cast in simple plaster moulds from slip with a specific gravity of 1·819 made in the ordinary way by blunging the materials together with water containing a small proportion of sodium carbonate and sodium silicate.

M. L. Bell and E. T. Montgomery have found that the following give good results with American materials:—

TABLE CV.—AMERICAN "MARQUARDT" PORCELAINS.

	M. L. Bell.			E. T. Montgomery.[1]
Georgian china clay	22	20	20	55
Tennessee ball clay	20	19	18	15
Flint	13	11	11	..
Felspar	24	22	21	..
Aluminium hydrate	21	28	30	..
Calcined alumina	..	..	..	30

Articles made of these mixtures are first burned at Seger Cone 2*a* (1120° C.) and then glazed at Cone 12 (1350° C.).

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[1] Termed by him a typical aluminous porcelain.

Bell has concluded that there should be less than 3 per cent. of lime, and very little plastic clay and free silica present. Alumina should be high; 20 to 30 per cent. in excess of that in the clay and felspar used appears to be essential.

A highly refractory Marquardt porcelain termed *Usalite* has been found to withstand continued exposure to temperatures above 1650° C. Articles of this material may be taken from a white-hot furnace into the cold air without cracking, and a cold steel rod may be placed on a Usalite tube at a temperature of 1100° C. without breaking the latter.

A careful comparison of these forms of Marquardt porcelain shows that they all approach sillimanite, Al_2SiO_5, in composition, and it is probably for that reason they are so refractory. (For further particulars about sillimanite articles see p. 385.)

Buchner's porcelain is composed of a mixture of clay and crystallised alumina (corundum). Unfortunately, it disintegrates on repeated firing at high temperatures, and has not fulfilled the expectations it raised.

Metallic oxides may be used singly, as sintered magnesia or alumina, which latter may be burned to a sintered refractory material without the aid of a bond if the temperature is sufficiently well controlled and the material is finely powdered. The temperature required is so high that only the smallest articles could be made until recently, but larger ones may now be made by fusing the oxide, casting it in simple moulds, annealing very slowly and finally grinding the article to the desired size and shape.

Metallic oxides may combine with each other to form spinels (p. 235), and the articles may then be made like spinel bricks (p. 508).

The use of spinels containing iron, chromium, zinc, copper, or titanium instead of magnesia for refractory materials has been patented by F. Engelhorn (Eng. Pat. 16,714—1906), the following mixtures being employed:—

1. Aluminium, iron, magnesium, and sodium oxides.
2. Aluminium, chromium, iron, and magnesium oxides.
3. Aluminium, chromium, iron, and zinc oxides.
4. Aluminium and copper oxides.
5. Aluminium and zinc oxides.
6. *Aluminium, chromium, silicon, and titanium oxides.*

He states that those containing magnesia and zinc are very resistant to alkalies, and those containing magnesia and chromium oxide are resistant to lime, cement, fluxes, glasses, etc. The most refractory compounds are Nos. 2 and 3. To bind the particles together he recommends the use of 10 to 20 per cent. of one of the following materials: clay, compounds of calcium, magnesium or aluminium, alkalies, glasses, or organic materials.

In a later patent (11,175—1907), Engelhorn uses mixtures consisting of alumina and oxides of one or more of the following: boron, silicon, arsenic, antimony.

A. A. Karyscheff (Eng. Pat. 2994—1907) uses the following mixture for refractory hollow ware:—

Natural spinel . .	35	parts powdered and 12 parts crushed.
Artificial spinel . .	78	,, ,, ,, 70 ,, ,,
Bond	16	,,
Boracic acid . .	0·35	,,
Naphtha residue . .	1	,,
Boiling water . .	6	,,
Calcium fluoride . .	0·5	,,
Lamp black . .	0·15	,,

According to A. T. Malin (U.S. Pat. 1,081,542), a suitable glaze for refractory ware composed of fused alumina bonded with clay consists of—

Felspar	41·8 per cent.
Flint	27·3 „
Whiting	17·7 „
Clay	13·2 „

In 1909, W. D. Coolidge patented the use of alumina bonded with tar or paraffin, the mixture being moulded whilst warm and subsequently burned *in vacuo* at 1400° C. to 1500° C. This should produce a material similar in many respects to Marquardt's porcelain, but somewhat more refractory.

Mixing.—To be successful, the non-plastic materials used in the manufacture of a refractory porcelain must be calcined repeatedly at an extremely high temperature; they must then be very finely ground and mixed as perfectly as possible.

Methods of Manufacture vary so much with the particular articles to be produced that they cannot be given in detail here. In brief, basins, crucibles, and other hollow ware are cast by making the materials into a slip, pouring this into porous plaster moulds and then pouring away the superfluous slip. Tubes and pipes may be made in the same manner, but are usually obtained by expressing the paste through a die, as in the manufacture of pipes or saggars.

For sparking plugs and electrical insulators, the semi-dry process is used for shaping or a slip may be made and the article cast. For dry-pressing, some of the steatite should be calcined before use, so as to prevent undue sticking to the moulds.

The best firing temperature is Seger Cone 10 to 14; suitable glazes[1] are:

$$\text{Glaze A}\quad \left.\begin{array}{l} 0{\cdot}210\ Na_2O \\ 0{\cdot}290\ CaO \\ 0{\cdot}500\ PbO \end{array}\right\} \left.\begin{array}{l} 0{\cdot}184\ Al_2O_3 \\ 0{\cdot}340\ SnO_2 \end{array}\right\} 2{\cdot}50\ SiO_2.$$

$$\text{Glaze B}\quad \left.\begin{array}{l} 0{\cdot}317\ K_2O \\ 0{\cdot}683\ PbO \end{array}\right\} \left.\begin{array}{l} 0{\cdot}131\ Al_2O_3 \\ 0{\cdot}230\ SnO_2 \end{array}\right\} 2{\cdot}39\ SiO_2.$$

They are fired at 950° to 960° C.

English manufacturers of refractory porcelains usually fire the ware, then glaze it and fire it a second time, but French manufacturers, who are far more numerous and work on a much larger scale, apply the glaze to the raw ware and only fire the goods once. The glazes used are those commonly employed for other varieties of porcelain, the fusibility being adjusted to suit the body to which they are applied.

When a porcelain-mixture is heated, the felspar fuses first, together with any "impurities" of similar fusibility. The molten glass so produced gradually dissolves the finest particles of clay and later the free silica. When the ware cools, mullite (derived from the solution of the decomposed clay in the molten mass) crystallises out, usually in a mass of felted needles. If the heating is unduly prolonged, even at a suitable temperature (1400° to 1500° C.), the whole material will be melted and on cooling will consist almost wholly of an amorphous glass in which mullite needles are embedded.

The burning is effected in saggars, in round up- or down-draught ovens, care being taken to raise the temperature steadily and slowly and to maintain it at the finishing-point for a sufficiently long time. This "soaking"—preferably in a slightly reducing atmosphere—is necessary in order that the ware may be uniformly vitrified. The cooling must be effected as cautiously as the heating.

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[1] L. E. Thiess, *J. Amer. Cer. Soc.*, 1937, **20**, 212.

Porcelain tubes should be fired whilst suspended in a vertical position so as to prevent warping. They should be weighted at their lower ends by a piece of clay which can be sawn off afterwards. If unglazed, such tubes may be covered with sand and fired in saggars.

When the ware is to be glazed, it is first burned as described above, and, after the glaze has been applied by "dipping," the ware is again burned at a suitable temperature, but at a more rapid rate, as very slow heating is detrimental to the glaze.

In Germany, the methods used for manufacturing refractory porcelains differ slightly from the English practice; the principal variations are that German manufacturers (*a*) temper the materials in an edge-runner mill instead of pugging them; (*b*) age the paste for a considerable time before using it; (*c*) cast more efficiently and with greater skill; (*d*) fire the biscuit ware at a much lower temperature; (*e*) fire the glazed ware at a much higher temperature (Cone 12 to 16); (*f*) make exceptionally large allowances in the moulds for deformation of the ware in the kiln; and (*g*) keep a reducing atmosphere in the kiln throughout the burning.

Grinding and mixing in a pan mill is superior to the use of rollers and a pug mill, as less air is introduced into the paste and the product is more uniform.

The use of the de-airing process (p. 564) appears to be advantageous.

Properties.—The chief characteristics of porcelains are those of a dense or vitrified body with a glassy fracture and some translucency, but the more refractory porcelains have a slightly porous body on account of the difficulty of burning them harder without distortion and are only feebly translucent.

The best qualities of porcelain should show no staining—even on examination with a lens—when either the whole article or a fragment is immersed in a 0·5 per cent. solution of eosin[1] for eighteen hours and afterwards rinsed and dried.

According to R. Rieke,[2] Berlin refractory porcelain has the following characteristics:—

The *colour* is intensified on heating, but returns to the original tint on cooling.

The *density* diminishes during burning; it is 2·64 for unglazed porcelain at 950° C. and 2·46 for the same ware when fully burned (1420° C.).

The *crushing strength* of 2·5-cm. cubes averages (according to Rosenthal) 4200 kg. per sq. cm. No direct figures for *tensile strength* are available; they probably resemble those for Hermsdorf porcelain, viz. 1300 to 2000 kg. per sq. cm. The same remark applies to the *modulus of elasticity*; that for Hermsdorf porcelain is between 5000 and 7000.

The absolute *heat conductivity*, or number of calories escaping in one second from a surface of 1 sq. mm. with a temperature difference of 1° C., is rather greater than that of glass and may be assumed to be between 0·002 and 0·004.

The *specific heat* of unglazed Berlin porcelain, according to W. Steger, is 0·202 between 20° C. and 200° C., and 0·221 between 200° C. and 400° C.

The *coefficient of expansion* of unglazed Berlin porcelain (according to Rieke)—

between 23° and 200° is 0·00000343
,, 23° ,, 400° ,, 0·00000353
,, 23° ,, 600° ,, 0·00000355
,, 23° ,, 700° ,, 0·00000356

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[1] Ordinary red ink does quite as well.

[2] *Zeitsch. angew. Chem.*, 1915, 72, 374–37

and according to F. Henning—

between 16° and 191° is 0·00000177
" 16° " 250° " 0·00000336
" 16° " 500° " 0·00000364
" 16° " 1000° " 0·00000434

The coefficient of expansion is, therefore, less than that of ordinary glass.

A thin, transverse section of the porcelain, when examined under the microscope, with a magnification of 300 diameters, should show a good development of mullite crystals. To secure this, a burning temperature of 1400° to 1425° C. is required.

An *ideal porcelain* for refractory purposes would appear to consist wholly of mullite, $3Al_2O_3.2SiO_2$. Both Marquardt's and Malinovsky's porcelains differ considerably from this.

The properties of *steatite porcelains* (p. 715) differ from those of true porcelain; their refractoriness seldom exceeds Seger Cone 15; their toughness is attributed to the crystalline magma, but this only applies to steatite fired at a very high temperature. Ordinary steatite porcelain contains 40 to 60 per cent. of glass and little crystalline matter. The coefficient of linear expansion of vitrified steatite is $7{\cdot}5$ to $8{\cdot}3 \times 10^{-6}$, so that this ware is liable to spall, though articles cut from natural steatite are not.

The *resistance to sudden changes of temperature* of articles of refractory porcelains may be tested by heating them for several hours at 950° C. to 1000° C., and then placing them on a sheet of cold lead or aluminium, after which they may be tested by means of eosin as described above. If the porcelain will resist this drastic test without being damaged, it may be taken as satisfactory, as no more sudden change in temperature is likely to be encountered whilst such articles are in use.

The *refractoriness* of Marquardt's porcelain is equivalent to that of Cone 38; it is very porous.

Berlin porcelain has no definite *melting-point*; when made into the shape of a Seger Cone and heated, it bends at the same temperature as Seger Cones 30 to 31 (1680° C.). A rod 80 mm. long and 6 mm. diameter, supported at one end, began to bend at 600° C. and was markedly deformed at 900° C., but crucibles and short tubes, etc., if properly supported, can be used up to 1400° C. The glaze on the ware begins to soften at 950° C.

The *electrical conductivity* of cold Berlin porcelain is extremely low; it increases with the temperature, being 300 to 400 times as large at 80° C. and allowing an appreciable electric current to pass at 300° C. The electrical conductivity (reciprocal of the resistance in ohms) of a 1 cm. cube is, according to Dietrich,[1] $0{\cdot}25 \times 10^{-12}$ at 97·5° C. and $0{\cdot}26 \times 10^{-11}$ at 189° C., and, according to Goodwin and Mailey,[2] $0{\cdot}05 \times 10^{-6}$ at 400° C. and 1×10^{-6} at 1000° C. Pirani and Siemens[3] have observed an electrical resistance of $1{\cdot}7 \times 10^{-4}$ ohm per centimetre cube at 727° C. or a conductivity of 6×10^{-5}. E. Rosenthal found that plates 2·5 mm. thick will stand a current up to 40,000 volts.

The *dielectric constant* is 5·73 (H. Starke), as compared with 6·61 to 6·84 for soft felspathic porcelain.

Refractory porcelain should have the following properties:—

(i) High resistance to heat, so that it does not show any signs of fusion when heated to a temperature at which Seger Cone 30 bends.

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[1] *Physikal. Zeitsch.*, 1910, **11**, 187.

[2] *Phys. Rev.*, 1908, **27**, 322.

[3] *Zeitsch. Elektrochem.*, 1907, **13**, 969.

(ii) High mechanical strength when heated, so that it does not show any signs of bending or warping at the temperatures at which it is used.

(iii) It must not be damaged by sudden and repeated changes in temperature, as when a red-hot piece is plunged into water or is suddenly subjected to a cold blast of air.

(iv) It must be impervious to gases, acids, alkalies, and any other substances with which it may come in contact when in use.

(v) It should have a good heat conductivity (especially when used for pyrometers).

(vi) It may contain minute air-bubbles, but should be impervious to gases, both in the cold and at 1400° C., under ordinary atmospheric pressure.

(vii) When a freshly fractured surface is treated with an organic dye (eosin, p. 720), the latter should be entirely removed by washing.

(viii) The glaze must, of course, be sufficiently resistant to the materials which the ware is to hold, otherwise the articles will be useless. This may be tested by boiling caustic soda or sulphuric acid in them for some time and then determining the loss in weight.

An *ideal porcelain* for refractory purposes would appear to consist wholly of sillimanite, Al_2SiO_5, which is formed by heating an extremely finely ground mixture of 5 parts of china clay and 2 parts of calcined alumina to a temperature just short of fusion. Marquardt's porcelain and Malinovsky's "Malinite" correspond very closely to it. The same substance also occurs in the felspathic porcelains, the china clay and flint in these being dissolved by the molten felspar and forming felted crystals of sillimanite in a glassy matrix on cooling. The felspathic porcelains are, therefore, less refractory than the ideal porcelain just mentioned.

The following additional rough *tests* are valuable :—

(*a*) A porcelain vessel filled with water should be placed in the flame of a Bunsen burner. The water should be evaporated gently and the dry dish should then be heated by the full flame of the burner. If it is then allowed to cool, no cracking should occur.

(*b*) A little sodium carbonate should be placed in the weighed porcelain vessel to be tested, heated until the salt fuses, and maintained in a fused state for five minutes. After being allowed to cool and cleaned, the vessel should not have lost or gained more than a couple of milligrams.

(*c*) The article (*e.g.* a pyrometer tube) should be heated ten times to a temperature similar to that at which it will be used. When quite cold, it should not have altered appreciably either in shape or size.

(*d*) A thin transparent section when examined under the microscope with a magnification of 300 diameters should show a good development of sillimanite crystals. To secure this, a burning temperature of 1400° C. to 1425° C. is required.

CHAPTER XVII.

REFRACTORY MORTARS AND CEMENTS.

MORTARS for refractory brickwork and for lining furnaces are frequently known as "*Cements*" or "*Fire cements*," though these terms are misleading. They are used for joining firebricks and other refractory articles in a similar manner to that in which ordinary mortar is used in buildings, viz. to unite the structure into a mass which is sufficiently strong even at the highest temperatures at which it is to be used. They are also used as a wash or protective coating and for patching defects. Refractory mortars and cements must, therefore, have properties similar to the refractory bricks and blocks which they unite, though, for obvious reasons, it is preferable if, in the raw state, they are plastic like other mortar. It adds greatly to the strength of the brickwork if the mortar is slightly more fusible than the bricks themselves, so that it may form a partially vitrified bond between them. A mortar which is readily fusible is, however, objectionable and a source of weakness rather than strength.

For most purposes, the mortar may have the same refractoriness as the bricks or blocks to which it is applied. The higher the temperature at which it is to be used, the more refractory must be the mortar and the more carefully must it be prepared. It should shrink as little as possible and must be quite free from any tendency to spall, peel, or fall out of place. The joints in refractory work are necessarily less resistant to heat than are the bricks or blocks used, and, for this reason, the joints should be as few and thin as possible.

Some users of refractory materials are curiously careless as to the cement they employ, and, whilst insisting on the most stringent tests for the bricks, will spoil the structure by using an inferior cement. Hence, it not infrequently happens that bricks are considered faulty when the real cause of their failure is the use of unsuitable cement.

Ordinary lime mortar cannot be used in structures exposed to high temperatures, as it is readily fusible and the lime in it exerts a highly corrosive action on the brickwork.

There is no essential difference between:

(a) *Refractory mortars and jointing cements*, as both are used for the same purpose, viz. laying bricks.

(b) *Refractory cements, fire cements, compos*, and *refractory plastics*; all are used for coating brickwork in order to protect it from hot gases, flue-dust, flame, and other corrosives.

(c) *Refractory concrete* and either of the preceding classes, except that the term "concrete" is usually confined to a mixture of an aggregate with a hydraulic bond, which sets after it has been mixed with water. Some of the air-setting cements may rightly be regarded as refractory concrete (see p. 746).

Strictly, when a cement is mixed with an aggregate, the product is a concrete, but the term "cement" is often used very loosely. Nor is there any essential difference between any of the foregoing materials, except that the mortars have usually a softer consistency than the cements.

Refractory cements are of three chief kinds—*plastic cements, tamping mixtures*, and *dry cements.* The plastic cements are sold in the form of a paste ready for use, but the dry cements require to be mixed with water. The tamping mixtures are sold in the form of a very stiff paste or a granular powder, and the dry cements are sold in the form of a dry powder.

Some refractory cements are known as *air-setting cements*, because they set hard on exposure to air and do not require any heat. Such cements may be in the form of a paste which is sold ready for use, or in the form of a powder which must be mixed with water. Air-setting cements are so named because they can "set" and harden without the need of artificial heat, though they do this more rapidly and completely when heated.

In pasty air-setting cements, the setting agent is silicate of soda (water-glass), gum, dextrin, starch, or similar material, which hardens on exposure, with or without a bond which imparts strength at high temperatures.

In the dry air-setting cements, the bond is usually solid silicate of soda, Portland cement, *ciment fondu*, or an organic bond such as dextrin, sulphite-lye, or molasses. On heating to bright redness, the organic bond burns away, leaving (in the absence of any other bonds) a weak mass which increases in strength as the temperature rises, and some vitrification occurs. This weakness from 600° C. to 950° C. is inevitable with such bonds; it is less serious with sodium silicate, Portland cement, and *ciment fondu* than with organic bonds. A bond which only begins to act at 1000° C., or above, may also be present, though it is not usually necessary if Portland cement or *ciment fondu* is used.

Most air-setting cements are of the fireclay-grog-silicate or silica-cement type, described in Classes 2, 3, and 4 on pp. 726 to 730, with the addition, if necessary, of one of the setting agents mentioned above.

Plastic v. *Dry Cements.*—Plastic cements are more satisfactory for most users, because few have the necessary appliances to convert a dry powder into a perfectly uniform paste, and if the paste has to be mixed by hand before use, the final product is generally much less uniform than a mechanically prepared plastic paste sold ready for use. Hence, plastic pastes usually give the best results, though they cost more to prepare and also for carriage, because of the water present and the necessity for using air-tight drums or cans instead of bags.

For men accustomed to working with cement, on the contrary, a powder is preferable, not only because it is more economical, but because it is less likely to be overloaded with water-glass.

Composition.—The Institution of Gas Engineers' Specification [1] states that "cementing clay or 'fireclay mortar' shall be machine-ground and, at the discretion of the manufacturer, may contain a suitable proportion of fine grog; but in all cases the cement clay shall be suitable for the purpose of binding together the bricks, blocks, or tiles for which it is supplied, and shall be capable of standing the same test for refractoriness."

This specification is unsatisfactory in several respects, the chief of which are that it permits the use of material which will not adhere properly to brickwork or retorts, and that it excludes various cements which are valuable for refractory work. A wider specification is, therefore, desirable for general work.

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[1] This refers to the 1911 Specification; the last one published (1934) does not mention mortar.

This is all the more necessary, as many mortars or cements for refractory work are sold under fancy names at prices out of all proportion to their true value. In most cases, they are simple mixtures of readily obtainable materials, and undergo little or no treatment. Hence, they are readily matched after a chemical and a mechanical analysis.

Refractory cements and mortars are classified as:

Acid cements, including those made of fireclay or silica, or both, or of asbestos.

Neutral cements, chiefly those rich in chrome ore, mullite, sillimanite, or calcium carbide, but sometimes including spinel and olivine cements, though none of these is perfectly neutral. Neutral cements should not react with silica, fireclay, or magnesia bricks.

Basic cements—chiefly those made of magnesite or dolomite, but also including alumina.

Insulating cements—for use with heat-insulating bricks.

Super-cements—chiefly including those of greater refractoriness than most refractory cements. The term is loosely used and is often misleading. The cements most commonly called super-cement are " alumina cements," " carbide cements," " sillimanite cements," " mullite cements," and " spinel cements."

High-temperature cements may be described in the same terms as " super-cements" ; *i.e.* they have a low bonding strength, but the highest practicable refractoriness. They are chiefly made of highly refractory, non-plastic materials with a minimum proportion of bond. See also " Basic Cements," " Alumina Cements," and " Spinel Cements." The refractoriness of high-temperature cements depends very largely on the bond, which is necessarily more fusible than the aggregate or it would not bind at high temperatures. It is of little use to employ a highly refractory aggregate, such as alumina, if the bond is to be a readily fusible one like silicate of soda or Portland cement. It would be cheaper and equally effective to use a less refractory aggregate.

Vitrifiable cements, *i.e.* those which become vitrified when in use and tend to adhere better and to be stronger than more refractory ones, but are less resistant to heat and, if overheated, tend to flow away, leaving an unprotected surface.

When the temperature at which they are used is not excessive and their refractoriness need not be considered, their great adhesion and, sometimes, their resistance to slag, are of great value. They consist essentially of refractory cements to which a flux has been added. In this class are included:

(*a*) Fireclay cements containing borax, felspar, Cornish stone, or other flux. As far back as 1877, F. T. Woodcock patented a furnace cement composed of 40 parts of fireclay, 20 parts of sand, and 3 parts of borax. The borax is seldom necessary and would normally be a disadvantage, inasmuch as it makes the cement more fusible. A mixture well known in Germany is composed of: fine sand 120, litharge 225, and calcined borax 200 parts, with sufficient water to make it into a paste. Many refractory cements contain boric acid or borax in some form. By beginning to fuse at a low temperature (900° to 1000° C.), such cements enable the mass to adhere to the brickwork more strongly than in those cements which are without borax, though with an appreciable loss of refractoriness.

(*b*) Aluminous cements to which a flux has been added and those in which a flux occurs naturally, *e.g.* in the form of *ciment fondu*.

(*c*) Cornish stone and water-glass (see " Special Cements ").

Special cements—a term chiefly applied to those cements mentioned in

Patent Specifications and recipes, which cannot be classified otherwise. Few of these special cements are of much value and it is unnecessary to describe them, as most " novelties " are of little use as fire-cements. An interesting example of a special cement which has proved useful at 1280° C. is a mixture of Cornish stone 80 to 90 and water-glass 10 to 20 parts. The Cornish stone vitrifies at about 1300° C. and the water-glass forms a useful bond at lower temperatures. The stone is too expensive for many purposes, but the mixture is sometimes useful where a vitrifiable cement is required. A similar cement, composed of 85 to 90 per cent. of crushed quartzite and 10 per cent. of felspar—sometimes with 5 per cent. of sodium fluoride—has been sold for some years in Germany under the name of " Höchst cement." The Russian "Andesite cement " and " Idamite " are of a similar nature.

This classification is not exact, but it serves a useful purpose, because it is important that the cement or mortar should have the same general properties as the articles it unites. Thus, fireclay bricks are acid in character and must not be laid in basic cement.

All refractory cements consist essentially of two parts: (i) the aggregate, and (ii) the bond, though this is not always recognised. The *aggregate* should be as refractory as practicable, as on it the refractoriness of the cement as a whole largely depends.

With a suitable aggregate and a suitable bond, the range of composition can be very wide, so that whilst many kinds of refractory cement are possible they all consist essentially of an aggregate, or skeleton, and a bond which unites the particles of aggregate and holds the whole in place.

The chief *aggregates* are: grog, dead-burned magnesite, dead-burned chromite, mullite (including sillimanite, cyanite, and the like), dead-burned bauxite, and other forms of calcined alumina (including the electrically fused material sold under such trade-names as " corindon " and " alundum "). Zirconia and silicon carbide (" carborundum ") are sometimes included in this class (see also " Aluminous Cements," " Basic Cements," and " Spinel Cements ").

The *bond* is necessarily more fusible, but care should be taken to avoid excessive fusibility and the production of a " thin " mobile fluid which causes the cement to drop out of place.

The following are the materials chiefly used as mortars or cements for refractory work:—

1. *Raw fireclay* ground so that it passes completely through a No. 24 sieve. This is plastic and refractory, but shrinks excessively when in use.[1] The fireclay should contain as large a percentage of combined alumina as possible.

2. *Sand* or *crushed silica* is refractory and does not shrink, but it is deficient in binding power. Some forms of silica, including some ganister, Klebesand, and some natural mixtures of silica and clay, become slightly plastic when tempered with water and so can be used without any admixture. Most sand is inferior to crushed silica rock, because sand-grains are usually too rounded to interlock well.

Raw silica rock is also more refractory than old silica bricks, but the latter have usually a constant volume, whereas the raw rock expands about 16 per cent. when heated. This expansion may be said, in one sense, to balance the shrinkage of the clay, but the changes do not occur simultaneously. Burned ganister or quartzite, which is afterwards crushed, is the best aggregate for this kind of cement, but the burning must have been sufficiently prolonged

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[1] Some clays are so rich in sand that they form natural mixtures. These really belong to Class 5 (p. 730).

The grading of the silica rock varies very greatly, from a simple material which passes completely through a 20-mesh sieve, to a complex one consisting of six or more grades, such as:

Through	Per cent.
30-mesh	99–100
40 ,,	93– 99
60 ,,	66– 80
80 ,,	55– 82
100 ,,	47– 71
200 ,,	28– 48

Some users prefer a ganister whose grading consists of:

Through	On	Per cent.
40-mesh	60-mesh	40
60 ,,	80 ,,	20
80 ,,	..	40

In English Patent 405,527 the grading is specified as:

Silica of 0·08–0·12 inch	30 per cent.
Silica of less than 0·24 inch	70 ,,

The composition of silica cements varies within very wide limits because the aggregate may be a mixture of silica rock and grog, or of silica bricks and fireclay bricks, or a chrome ore and silica, or carborundum and silica in many different proportions.

3. *Mixtures* of raw and burned fireclay (clay and grog, p. 139) are excellent in every way, if the proportion of grog is sufficient to prevent shrinkage, though this is seldom the case. Hence, this class of mortar usually shrinks considerably, though not so much as raw fireclay alone. The proportion of grog added varies from one-quarter to twice the weight of the clay, equal measures of ground fireclay and grog being very convenient and satisfactory.

One of the best-known German cements consists of equal volumes of grog and fireclay. Mixtures containing carborundum, ganister, etc., are mentioned later under their respective names.

Among the many *air-setting cements* in this class are:

Mixture.	Fireclay, per cent.	Grog, per cent.	Silica-rock, per cent.	Water-glass, per cent.	Water, per cent.
A	30	55	..	15	9
B	30	45	..	25	5
C	25	50	..	25	5
D	50	50	..	..	10
E	65	35	..	..	10
F	70	..	20	10	8
G	..	45	45	10	8
H	70	25	..	5	12
I	25	50	25	..	10
J	15	..	85	..	10
K	37	13	37	13	10
L	18	72	..	10	10

The following are not air-setting if mixed with water alone, but become so when mixed with a suitable proportion of water-glass or syrupy silicate of soda and water:—

Mixture.	Fireclay, per cent.	Grog, per cent.	Ganister, per cent.	Water, per cent.
M	25	50	25	10
N	15	15	70	10
O	10	45	45	10
P	10	20	70	10
Q	10	70	20	10
R	10	30	60	10

On the whole, the cements without water-glass are the most heat-resisting, but the presence of a little water-glass makes a stronger cold joint before heating and so is convenient for some purposes. The use of 25 per cent. of water-glass (as in B and C) is excessive for a high-class cement, as 20 per cent. of water-glass will lower the refractoriness of a cement from Cone 32 to Cone 26 (1710° to 1580° C.).

Air-setting cement-pastes sometimes set hard in the container, *i.e.* before they are used. This is due to part of the water evaporating—usually as a result of a badly fitting lid. This tendency may be diminished by replacing part of the water by *glycerine* or by using *oil* instead of water. English Patent 318,696 specifies the following mixture:—

Carborundum	100 parts
Water-glass	40 ,,
Glycerine	20 ,,
Castor oil	2 ,,

This would be very expensive.

Opinions differ greatly as to the respective merits of grog and silica and mixtures of these two, but experimental work has clearly shown that:

(*a*) A mixture of grog and silica may be cheaper than grog alone, but it is often less refractory than either grog or silica alone.

(*b*) Any clay in excess of that actually needed is objectionable on account of its shrinkage.

(*c*) Any flux reduces the refractoriness, but this disadvantage may be more than balanced by the gain in strength at 600° to 1000° C.

(*d*) The grog must have been sufficiently burned. It is customary to use broken firebricks, and there is no objection to them if they are clean and free from a serious proportion of fused material. It is generally found, however, that grog made by burning lumps of fireclay is better than that made by crushing firebricks, as the former breaks down into more angular particles, which have a better bonding power. The grains in crushed firebricks are more rounded and tend to produce a weaker mass. For some purposes, grog which is not burned too hard is best.

(*e*) The size of the particles of grog or other aggregate is important. The sizes vary very greatly; it seems best to have three sizes of grog:

Coarse grog—through 20-mesh, retained on 40-mesh—below 15 per cent.
Medium ,, ,, 40 ,, ,, ,, 80 ,, ,, 25 ,,
Fine ,, ,, 80 ,, above 60 ,,

For some purposes, the proportion of medium-grade may be increased to 60 per cent. and the fine-grade reduced to 25 per cent. If the grog is too fine, the cement will tend to spall. For this reason, the proportion of grog passing 120-mesh should not usually exceed 20 per cent.

Where great resistance to slag is required, the proportion of fireclay should be rather high.

The grading of the cement as a whole is quite as important as that of the grog. There should be at least 45 per cent. of the whole cement capable of being washed through a 200-mesh, or the cement will be too short and rough unless it is required for very large work. In most cements, not more than 10 per cent. should remain on a 40-mesh sieve; for coarse cements not more than 10 per cent. should remain on a 20-mesh sieve.

A very popular cement of this class consists of equal parts of grog and siliceous fireclay (80 per cent. silica), the whole material passing through a 30-mesh and 50 per cent. of it through a 200-mesh sieve. To increase the workability of the mixture, 3 to 10 per cent. of bentonite may be added in place of an equal weight of clay. This is only necessary where a very " short " clay has to be used. A washed fireclay or a good ball clay is to be preferred to bentonite.

A temporary bond should not be needed in a fireclay cement, though one is sometimes used.

Grog cements are those in which the aggregate is composed wholly of grog (p. 140), the bond being fireclay or any other suitable material. There is evidence that cements made of grog and bentonite (5 per cent. maximum) or grog and ball clay (15 per cent. maximum) are stronger than cements made of grog and fireclay at all temperatures up to about 900° C.; no determinations of the strength above this temperature have been published. For information on cements made of grog and *ciment fondu* see " Refractory Concrete," p. 746.

A mixture of ground china clay and fireclay is sometimes used as a mortar in frit-kilns.

A mixture of 5 parts of asbestos with 95 parts of clay was patented by Hutcheson and Service in 1898. So small a proportion of asbestos has little value; a larger proportion—up to 30 per cent.—is often useful where a fibrous material is required. Although asbestos has the advantage of forming a felted mass which holds the particles of clay together, it decreases the heat-resistance of the material at high temperatures. R. M. Howe found that the presence of only 9 per cent. of asbestos reduced the refractoriness of a fireclay from Cone 30 to Cone 18.

Carborundum may be added to fireclay without appreciably reducing the refractoriness.

4. *Mixtures* of sand, firebrick, or crushed silica rock and lime or Portland cement meet many requirements, provided no more lime is present than is necessary. Such mixtures are sufficiently plastic and refractory, and the shrinkage is so slight as to be negligible. Some mixtures of this type, containing about 1½ per cent. of lime or 3 per cent. of Portland cement, form exceptionally good cements in firebrick work. They have little or no contraction in use; they have a good bonding power before being heated and a still higher one in use. With care, they can be made of ample heat resistance for all ordinary purposes, the makers of one well-known brand claiming that it has a heat resistance of 1800° C. On the other hand, R. M. Howe found that the refractoriness of a fireclay was reduced from Cone 30 to Cone 15 by the addition of 10 per cent. of Portland cement.

H. Spatz (Eng. Pat. 7736 of 1904) suggests the use of a mixture of equal parts of lime and chemical wood cellulose lye (" sulphite liquor ") mixed with about 84 times its weight of sand, crushed quartz, or other material. In some cases, 3 parts of lye, 1 part of lime, 7 parts of water, and 42 parts of sand or other non-plastic material, may be substituted.

Cements consisting of crushed silica and lime are improved in bonding power at high temperatures by the addition of a little fireclay or bentonite, but not by small additions of ball clay.

A mixture of ground grog with one-tenth of its weight of Portland cement has proved highly satisfactory in some cases, though the objection applicable to the use of any lime compound—great fusibility—applies equally to such a mixture.

A greatly improved product is obtained by using *ciment fondu* (aluminous cement) instead of Portland cement (see "Refractory Concrete," p. 746), because Rankin's ternary diagram shows that any reaction between aluminous cements and grog leads to the formation of high-melting eutectics, whereas Portland cement gives easily fusible materials. The rapid hardening of aluminous cement enables its full refractory properties to be utilised 24 hours after application. Temperatures up to 1400° C. may be withstood with suitable aggregates and the optimum cement-content.

5. *Silica cements*, consisting chiefly of sand or crushed silica rock and fireclay, lime, or other bond.

Silica cements for steel-furnaces should usually consist of particles of the following sizes:—

	Range, per cent.	Average, per cent.
On 20-mesh	4–6	5·2
20- to 30- ,,	5–13	7·2
30- to 60- ,,	14–43	26·1
60- to 90- ,,	11–25	16·7
through 90- ,,	27–54	44·8

The average specific gravity of the silica used is 2·6 to 2·65, but it is better to use burned silica (from clean silica bricks), in which the quartz has been converted into cristobalite or tridymite and the specific gravity reduced accordingly.

Cements composed of silica bricks and clay are largely used, and whilst some neither shrink nor expand appreciably when heated, the fact that they consist of two entirely different materials which do not combine is a disadvantage, and when such a mixture is required it is better to use grog instead of silica.

In 1913, T. B. Rogerson patented a furnace cement of this type, consisting of 5 parts of broken silica brick, 2 parts of silver sand, and 3 parts of refractory clay. For a finishing coat, equal parts of the sand and clay are specified.

In silica cements composed of silica and fireclay, the proportion of clay varies between 20 and 45 per cent. In the United States, the cements made of crushed quartzite and clay usually contain 15 to 35 per cent. of clay. It is common practice to substitute for half the quartzite an equal amount of silica bricks. The advantage of clay-bonded silica cements is that they have a higher refractoriness-under-load than have clay-grog cements, and are more resistant to slags. A mixture of grog, silica, and fireclay appears to be better than any two of these substances.

A refractory cement composed of fused quartz with 1 to 10 per cent. of kaolin was patented in 1931 (Eng. Pat. 373,796).

Instead of fireclay, other bonds may be used (see p. 736), these including:

(i) Hydrated lime (1½ to 3 per cent.).

(ii) Bentonite (3 to 6 per cent.), which has a good " floating " action and is an aid to smooth working.

(iii) Ball clay (5 to 15 per cent.), preferably added in the form of a slip, which produces very good cements resistant to almost any temperature.

(iv) Silicate of soda (3 to 4 per cent., corresponding to 1 per cent. of Na_2O), which is useful as a temporary bond as well as a bond at moderate and higher temperatures.

(v) Various temporary bonds, of which sulphite-lye, molasses, and dextrin are the most popular. These burn away at a red heat.

A temporary and a permanent bond, or two permanent bonds, may be used simultaneously.

All these bonds should be very finely ground, unless (as in the case of clays) the particles have been separated by making them into a slip and screening off the coarser ones.

The addition of 0·05 per cent. of sodium carbonate and 0·10 per cent. of gum-arabic, or gum-karaya, makes a silica cement work more smoothly under the trowel, but either substance without the other seems to be of little value.[1]

In silica cements devoid of clay, it is advisable to keep the proportion of alumina below 5 per cent., or a eutectic of low melting-point may be formed.

The linear shrinkage on drying should not exceed 2 per cent., and on firing the dried cement it should not exceed 1½ per cent.

Silica cements have a high refractoriness, but they are very liable to spall, and there seems to be no means of preventing this other than by using an aggregate of fused silica, which is much too costly for general use.

6. *Magnesite and dolomite cements* are usually made of dead-burned magnesia (or dolomite) crushed to a powder and mixed with a bond. Sometimes old magnesite (or dolomite) bricks are used instead of new material. The *bond* may be tar, light magnesia, a solution of magnesium chloride, or magnesium sulphate (Epsom salts), *ciment fondu*, starch, molasses, or sulphite-lye. A useful mixture consists of:

Dead-burned magnesite (60- to 80-mesh)	90 per cent.
Plastic (caustic) magnesia (80- to 100-mesh)	10 ,,
Magnesium chloride solution (15° Bé)	sufficient to form a paste.

Water-glass must not be used with magnesia or dolomite, as it sets too quickly.

For laying basic bricks, the magnesium or dolomite powder is sometimes made into a soft paste with water and no bond is added; for coating brickwork or for patching, a bond must be used. (For further information on bonds see p. 736.)

A basic refractory cement developed in Canada consists of a dolomite containing 3½ times as much magnesia as lime, to which has been added about 7·5 per cent. of iron oxide or chromium oxide, sufficient silica to form dicalcium silicate and sufficient sodium silicate to form a temporary bond. The plasticity may be increased by adding a little fine chrome ore. Sometimes silica or alumina is added to the magnesia, as in Eng. Pat. 481,281 (1936), in which a mixture of lime, silica, and magnesia is heated to form merwinite and calcium orthosilicate, the product, when ground, forming a refractory cement which sets when mixed with water.

Natural or synthetic olivine (forsterite, $2MgO.SiO_2$) makes a good refractory cement for magnesite, forsterite, and chromite bricks.

Magnesia and dolomite cements should have a very low porosity, or they will absorb iron too readily and are then soon destroyed.

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[1] Cole, *J. Amer. Cer. Soc.*, 1935, **14**, 2, 61.

7. *Chrome cements* usually consist of chrome ore or crushed chrome bricks, with a little fireclay to act as bond. They are also made of a mixture of dead-burned magnesite and chrome ore, with fireclay or other bond. Any of those mentioned on p. 736 may be used; *ciment fondu* is also quite satisfactory (see Eng. Pat. 304,492). Some users have found that water-glass and other forms of sodium silicate are not satisfactory in chrome cements.

Only the hard ore (hardness 5 to 6) should be used, the crumbly ones being useless in cements. The ore should pass completely through a 40-mesh sieve, but it should be almost free from dust, or the cement will crack when in use.

Sometimes a little flux (felspar) is added, but usually the impurities in the chrome ore are sufficient to cause the cement to adhere if it is applied with sufficient force.

For application as " hot patching " to retorts, Clews, Booth and Green[1] found the best chrome cements (in the order shown) to be composed of:

Silica cement	80	80	82 parts
Iron chromate	20	..	.. ,,
Chrome ore	..	20	.. ,,
Potash felspar	..	..	18 ,,

Three other chrome-silica cements which have given satisfactory results are composed of:

Chrome oxide	20	40	80 per cent.
Ganister	80	60	20 ,,

The following recipes show how variable is the composition of commercial chrome cements:—

	A.	B.	C.	D.	E.
Chrome ore	94	93	88	92	70
Bentonite	5	2	..	..	..
Gum-arabic	1	2	..	..	..
Chrome alum	..	3	..	..	..
Sodium silicate at 28 oz. per pint	..	..	12	..	..
Sodium silicate (powder)	..	..	..	8	5
Clay	..	..	..	..	25

Of these, A is the best, B is rather " short," C and D are slightly less refractory but very hard and strong in use, and E is similar to C but is more easily spread.

The use of a mixture of chrome ore, dry silicate of soda, and an organic bond is claimed in Eng. Pat. 240,277.

A mixture of:

Ganister	80 parts
Chrome ore	20 ,,
Lime	1½ ,,
Sulphite-lye	10 ,,

in which all the ganister passes through a 40-mesh and 40 per cent. of it through an 80-mesh, whilst all the chrome ore passes through a 100-mesh, is useful for temperatures up to 1350° C. Chrome cement can be used for laying firebricks and is specially useful where thick joints must be employed. It has the advantage of having a very small shrinkage.

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[1] *Trans. Cer. Soc.*, 1936, **35**, 5, 264.

It is usually advisable for furnace builders to purchase chrome cements ready-made, as their preparation requires a considerable amount of skill as well as special machinery.

8. *Alumina cements* may be made of almost any form of calcined alumina and a bond, but the most refractory are those in which fused alumina is used. The usual bond is a fireclay, ball clay, or plastic kaolin, the minimum proportion necessary for a good working consistency being used. The use of a mixture of fused alumina and *ciment fondu* was patented in 1926 (Eng. Pat. 276,185).

Kestner cement [1] is composed of: bauxite, calcined at 1700° F., 2 parts, refractory grog 3 parts, and *ciment fondu* 1 part.

The corresponding German Patent (438,264—1925) specifies grog 2 parts and *ciment fondu* 1 part.

With some forms of fused alumina, the grains are so smooth that the bond does not adhere satisfactorily, and this causes some users to prefer a cement in which hard-burned bauxite (1400° C.) is preferred to fused or sintered alumina. Care should be taken to avoid alumina of poor quality, which is offered at a low price. Alumina cements may have a refractoriness equal to Seger Cone 37; the aggregate can be crystalline alumina or a mixture of mullite and corundum, non-porous and non-absorbent, and the cement should have a negligible shrinkage.

For most purposes, the cement should be free from particles which will not pass through a 50-mesh sieve.

9. *Sillimanite, mullite, and similar cements* are made of calcined (1500° C.) cyanite, "sillimanite," mullite, diaspore, or andalusite, with a bond composed of slaked or hydrated lime, bentonite, fireclay, ball clay, china clay or *ciment fondu.*[2] Silicate of soda should not be used for the most refractory cements of this type. The proportion of bond should not be more than is needed to secure a fair workability; as the bond is less refractory than the aggregate, it should seldom exceed 30 per cent., though cements composed of equal parts of clay and aggregate are often used.

For most purposes none of the aggregate should be larger than will go through a 40-mesh sieve.

The refractoriness of cements of this class should not be less than Seger Cone 20 (1530° C.). They are usually made of various grades, the coarsest being for "large" work and the finer ones for coating and for small work.

10. *Carbide cements* are composed of silicon carbide ("carborundum") with a bond of fireclay or water-glass, though the other bonds mentioned on p. 736 may be used. Some organic bonds cause cements containing carbides to blister when in use. The blistering is only superficial and is usually harmless.

Typical mixtures for carbide cements are:

Silicon carbide	82	85	60	80	90	75
Fireclay	18	15	17	15	..	25
Grog	..	..	23	..	..	..
Temporary bond	..	..	..	5	5	..
Chrome ore	..	..	..	..	5	..

A good refractory cement can also be made of 3 parts of carbide to 1 part of *ciment fondu.*

One of the patents is that of L. E. Müller, who in 1904 patented the

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[1] U.S.A. Pat. 1,573,072 (1926).

[2] When a clay bond is used it is often an advantage to include a small proportion of raw cyanite in the mixture, so as to counterbalance the shrinkage of the clay.

following mixture: "90 to 60 parts of carborundum, 10 to 40 parts of fireclay, 0 to 4 parts of lime, and 20 to 50 parts of silicate of soda solution of specific gravity 1·48." The wide variations possible in this recipe make it almost useless except as a mere outline.

The following mixtures have been used for repairing retorts:—

	A.	B.	C.
Carborundum	3	6	1 parts
Fireclay	1	1	1 part

In some cases, it is preferable to add sand and powdered glass, as in the following mixture, which is used extensively in the United States for repairing cracks in glass pots:—

Carborundum	1 part
Fireclay	2 parts
Sand	1 part
Powdered glass	1 ,,

For lining iron vessels which are constantly kept hot, a mixture of carborundum 3 parts, and water-glass 2 parts, is sometimes employed. On cooling, the lining shells off, so that the furnace must constantly be heated.

The use of *firesand*, a by-product of the manufacture of carbides, is not recommended except where a better cement is not needed. It has been used satisfactorily in the Royal Mint (with water-glass as a bond) as a wash for the interior of furnaces. It has also been used for mending saggars.

Some manufacturers use a mixture of ganister and carbide, but this is objectionable. The ganister reduces the effectiveness of the cement and is merely a diluent. A much better cement is made of a mixture of fused alumina, or fused diaspore, and silicon carbide, with a fireclay bond.

Carbide cements are valuable because of their greater heat-conductivity and their great strength when in use. They are most stable under reducing conditions. When heated in air, the carbon tends to burn away and the resultant silica to fuse. If the heat-effect is only superficial, the fused silica seals the pores and prevents further decomposition, so that such cements are often more durable than would be anticipated from laboratory tests.

When tested, most carbides have a refractoriness equal to Cone 28 or 29, which is not so high as is usually imagined. The carbide aggregate decomposes below 1600° C., but, when in use, the cement often appears to withstand a higher furnace temperature.

A difficulty sometimes experienced with carbides is that the grains are so smooth that the bond will not adhere to them. It is essential to rub the clay on to the grains with some pressure, and a prolonged panning in an ordinary tempering mill or "wet pan" is the best method of ensuring ample adhesion. This is impracticable when *ciment fondu* is used as the bond.

11. *Spinel cements* are composed of some kind of spinel (usually magnesium aluminate, p. 235) and a fireclay, caustic magnesia, or other bond.

The use of equal parts of chromite, magnesite, and *ciment fondu* (all fine enough to pass through 100-mesh, or one-third of this fineness and the rest of the chromite and magnesite as larger particles) is claimed in Eng. Pat. 430,036. It is not claimed that a spinel is produced. These cements are almost new and little work has been done with them.

Spinel cements are nearly neutral and can be used with basic or acid brickwork at almost any temperature. They are very expensive.

12. *Olivine cements* contain an aggregate composed of olivine (natural magnesium silicate) or an artificially prepared olivine, made by heating magnesia and silica. They are not, at present, made in this country, but have attracted some attention in the United States. Olivines of sufficient purity and in sufficiently large masses are rare in this country. Olivine is not as refractory as the magnesia used for basic bricks, nor as refractory as a pure spinel, so that the use of olivine as an aggregate in cement is greatly restricted.

The following olivine cements have been patented in England: 260,296, magnesium orthosilicate (no binder mentioned); 301,547, olivine and 2 to 5 per cent. of silicate of soda; 307,391, olivine and clay; and 373,846, olivine, caustic magnesia, and magnesium chloride.

13. *Zirconia cement* consists chiefly of *calcined* zirconium oxide, ground sufficiently fine to pass through a 200-mesh sieve, with the aid of water, but various mixtures—some with only a small percentage of zirconia—have been sold as zirconia cements. Raw zirconia cannot be used as a cement, as it shrinks greatly on heating. If equal parts of raw and calcined zirconia (1300° C.) are used, the shrinkage is within permissible limits.

With very pure calcined zirconia, and a minimum proportion of ball clay, a cement can be used which will remain stable at 1550° C. It is easily attacked by slags, but is resistant to molten glass.

At one time zirconia cements attracted much attention, but are now seldom seen. The cost of the material is very high and is another cause for lack of interest in zirconia cements.

14. *Carbon cements* usually consist of tar, soft pitch or bitumen, to which finely ground grog or other refractory material may be added to impart "stiffness" and load-bearing power. Unless some such addition is made, the cement tends to crack.

Graphite cements are seldom made wholly of graphite, but usually by crushing old graphite crucibles and adding a little fireclay as a bond. The addition of graphite to other cements increases workability and is, usually, unobjectionable.

15. *Asbestos cements* were, at one time, very popular, but a few refractoriness tests soon showed that asbestos greatly reduces the heat-resistance of the cement, *e.g.* as little as 10 per cent. of asbestos added to a fireclay will reduce the refractoriness from Cone 30 to Cone 18. Asbestos is only of value when used in the form of fibres at least ½ in. long: it then acts as a reinforcement to the cement. Shorter pieces of asbestos and the "powder" are quite useless in this respect and should not be employed.

When the temperature to be attained is not above 1100° C., a mixture of equal weights of asbestos and water-glass is often very convenient for plugging hollows and fissures.

For moderate temperatures, the inclusion of 10 per cent. of long-fibred asbestos as a *reinforcement* is advantageous in some cements but not in high-temperature cements.

16. *Insulating cements* are chiefly made for laying insulating bricks. They usually consist of calcined diatomaceous earth or of highly porous firebrick (see "Insulating Bricks," p. 395) with sufficient fireclay, Portland cement, *ciment fondu*, or silicate of soda to form a good bond. They correspond to a refractory cement in which calcined diatomaceous earth or crushed porous firebrick has been substituted for the silica, grog, or other aggregate. Occasionally, asbestos or expanded mica is also used.

Insulating concrete can be made of calcined diatomite mixed with one-fifth of its volume of *ciment fondu*. The diatomite must be thoroughly soaked in water before adding the cement. The concrete has about half the insulating power of diatomite bricks.

17. *Special cements* are made for a variety of purposes. Most of them ar "secret" preparations and closely resemble some of the cements previousl mentioned. Others are of limited use; thus a mixture of equal volumes o sand and sulphur is very resistant to acid, but can scarcely be regarded as refractory cement (see p. 726).

Bonds for Cements.—Most of the bonds used in the manufacture of refractory cements are the same as those used in making refractory bricks, viz.

(*a*) Ball clay, china clay, or bentonite.

(*b*) Silicate of soda (including water-glass).

(*c*) Hydrated lime.

(*d*) Felspar, borax, calcium chloride, magnesium chloride, magnesium sulphate, or other flux.

(*e*) Various organic bonds (p. 419).

Of these bonds, *tar* is chiefly used for bricks of a neutral or basic character: thus, bricks made of magnesia or carbon are usually laid in mortar made of magnesia- or carbon-brick dust and tar. Occasionally, tar is used alone, but this is only successful where the joints are exceptionally thin.[1]

Water-glass, or sodium silicate,[2] is largely used for cements containing grog, powdered firebricks, or other similar materials. It is obtainable either in the form of a viscous liquid or powdered crystals. Potassium silicate is a similar substance, but is more readily soluble in water, and is thought, by some users, to be a superior binding agent.

In complex mixtures, the addition of water-glass need not be accompanied by any change in the proportions of the other constituents, a mixture of 1 part of silica or grog and 3 to 4 parts of clay being prepared in the usual manner, and then mixed with water-glass in the proportion of 1 gallon of the syrupy glass to about 3 cwt. of the dry mortar, sufficient hot water being added to give the mass the desired consistency. The materials are difficult to mix properly unless a suitable pan mill is used, and it is generally necessary to add various quantities of water during the mixing and to continue the treatment in the mill until a suitably plastic paste is produced. It is possible to dry the mixture if it cannot be used immediately or for transport to other countries, but it is far better to keep it in a moist state in air-tight drums.

A mixture containing water-glass is excellent for patching furnaces, etc., if care is taken to have the water-glass, grog, and clay in suitable proportions.

Great care is needed in using the dry silicate and metasilicate of soda, because of the difficulty of obtaining a completely homogeneous mixture.

The great advantage of water-glass in refractory cements is its power of "setting" at a very low temperature—so that the joint becomes firm as soon as it is dry—and its power of combining chemically with the brick-dust when heated and so forming a particularly strong bond.

Clay is so well known as a binding agent that its use in refractory mortars need not be described in detail. It is sufficient to state that the clay should be as plastic as possible, and only enough should be used to produce a cement of the desired plasticity. An excess of clay is detrimental on account of its shrinkage when heated.

The use of *sulphite lye* as a temporary bond is increasing, particularly on the Continent, as such materials keep the mortar in an adhesive state until

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[1] Molasses is sometimes preferred to tar.

[2] A cement composed of ground bricks and magnesium silicate moistened with a 1 per cent. solution of aluminium sulphate was patented by G. C. Fludder in 1909.

the temperature is high enough for the bond to be destroyed, after which the strength of the structure will depend on the formation of a bond of a vitrifiable nature. Usually, there is a long temperature-interval between the destruction of the adhesive and the formation of a vitrified bond, and during this stage of the heating there is always a risk of the structure collapsing unless great care is taken, but when once a suitable amount of vitrification has occurred the structure is again rendered safe. Water-glass and other soda compounds, by bridging this gap, are often regarded as invaluable, but their great drawback is the fluidity of the fused mass which they form; this militates against their successful use, in large proportion, at the highest temperatures.

Uses.—It is important to select a cement which is suitable for its intended purpose and one that will not damage any brickwork in contact with it.

For *fireclay bricks*, much the most suitable mortars and cements are those of the No. 3 class. They consist of a mixture of fireclay and grog in such proportions as will provide ample binding power with a minimum of shrinkage. The proportions vary with the clay used; if the latter is plastic it may suitably be mixed with about twice its weight of grog, or with an equal weight of grog and sand respectively. For some purposes, it is desirable to replace part or all of the clay with silicate of soda (water-glass) so as to produce a cement which hardens at a low temperature. A mixture of grog and *ciment fondu* is also satisfactory; it hardens rapidly without any heat (see "Refractory Concrete," p. 746).

For *silica bricks*, the mortar used to be a mixture of fine refractory sand and clay in the proportion of 9 parts of silica to 1 of fireclay, but preference is now given to unblended material, such as fine washed and ground ganister or ground quartzite, whilst some firms attach great importance to the use of crushed (old) silica bricks as mortar.[1] Silica cement usually contains from 83·30 to 94·90 per cent. of silica, 90 per cent. being a good average. The percentage of alumina varies greatly; it may be as low as 1 per cent. or as high as 12 per cent., whilst other substances vary from 2 to 6 per cent. The refractoriness varies considerably on account of the variations in composition, and usually ranges between Cones 26 and 32. According to R. J. Montgomery, the drying shrinkage of a silica cement should not be more than 2 per cent., and is preferably about 1·5 per cent., whilst the burning shrinkage should be very low up to Cone 13, after which it increases rapidly in proportion to the amount of alumina and flux present. Where only a very small proportion of clay is present, there may be no shrinkage, but a slight expansion due to the silica.

The porosity of silica cements decreases when they are heated to very high temperatures. At Cone 1, the porosity is usually about 30 to 35 per cent., but at Cone 20 it is only 15 to 30 per cent.

The specific gravity of silica cements also varies, being reduced from 2·40 to 2·45 at Cone 1 to 2·20 to 2·38 at Cone 20.

The hardness and crushing strength of silica cements is greatest at high temperatures, the cements fired at 1316° C. to 1538° C. having the maximum hardness when cold.

The cement should have the same refractoriness as the silica bricks. It should have the same expansion and contraction as the silica bricks so as to form an adhesive joint without cracks.

The disadvantage of using silica or sand without any bond is the weakness of the structure until a sufficient temperature has been obtained to secure

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[1] It is desirable to keep the proportion of clay as low as possible in the cement used for silica bricks, as a high proportion of alumina causes fluxing.

the partial fusion of the silica. This may be overcome by the addition of water-glass.

For *magnesia and dolomite bricks*, the mortar usually consists of about 9 parts of crushed magnesia bricks mixed with 1 part of hot tar, or 2 parts of light magnesia and sufficient water to form a stiff paste.

When refractory bricks, etc., are laid in tar or mixtures containing tar, the " mortar " should be hot enough to enable the articles to be placed properly.

Dead-burned magnesia, when ground to powder and mixed with water, sets in about twelve hours as hard as Portland cement, and resists water equally as well. A still better mixture consists of 4 parts of sintered magnesia and 1 part of light magnesia made into a stiff putty with water, and forms an excellent cement. When required in thick masses, it may be improved by working into it a moderately large proportion of long-fibred asbestos.

The Vietsch Magnesite Works (probably the most renowned makers of magnesia bricks), in 1913, patented a mixture consisting of 77 parts of dead-burned magnesia, 3 parts of lime-dust, 25 parts of iron turnings, and 20 parts of water.

In 1907, F. O. Werther patented the following mixture as a cement for magnesia bricks: Magnesia 60 parts, fireclay 20, chrome ore 5, silica 5, blast-furnace slag 5, basic steel slag 5, grog 5, salt 1, and Portland cement 1 part. These materials are worked into a paste with water containing treacle or other carbonaceous matter.

The following mixture was patented by J. E. Williams, in 1903, as a refractory cement specially suitable for repairing retorts: Magnesia is mixed with three times its weight of the following mixture—china clay 200 cwt., barytes 100 cwt., silicate of soda at 100° Tw. 40 gallons, water 24 gallons, and borax 28 lbs.

Dry Portland cement mixed with gas tar has been patented by A. T. Macfarlane (in 1902), and a mixture of Portland cement with 5 to 8 per cent. of starch by R. Middleton in 1903. Both these materials are highly basic, and may have an undesirable action on firebricks made of clay or silica especially at temperatures above 1200° C.

For *carbon bricks*, the mortar is usually a mixture of finely ground coke and sufficient (20 per cent.) fireclay to bind it into a plastic mass when water is added to the mixture.

For *chromite bricks*, it is desirable to use a mixture of ground chromite and sufficient clay or blende to bind it.

Cements specially suitable for patching *saggars* are: (*a*) fireclay 65, felspar 30, and litharge 5 parts made into a paste with water. The proportion of lead may be varied to suit the temperature at which the saggar is burned; (*b*) kaolin 1, fine grog 2, and red lead 1 part made into a paste with a mixture of equal parts water and water-glass. This cement is self-hardening, so that it is merely necessary to wet the broken saggar, apply the paste, tie a string round the saggar, and leave it in a warm place until the patch is hard; (*c*) a carborundum cement (see " Carbide Cements," p. 733).

Cements made on the same principle as refractory brick materials have been recommended by Fludder, and A. A. de Karyscheff (Eng. Patent 2994, 1907) has specified the use of a complex mixture of *spinels*.

Crucible cements are usually mixtures of clay with a little borax, water-glass, sand, or powdered glass, similar to those used for saggars and bricks. Sometimes " iron cements " are used for repairing crucibles. A strong waterproof cement that will stand high temperatures may be made by mixing powdered silica or fine sand and powdered silica with a solution of magnesium chloride of about 10 per cent. strength. This composition is applied as a putty and then painted or soaked in a solution of silicate of soda of about 30 per cent. strength. This forms magnesium silicate as a binding material for the silica.

Probably the best known cement for graphite crucibles is fireclay, which, with water, binds the graphite fairly well and itself stands high temperatures.

For *all-carbon* cements, tars or soft pitches are used, but they must be applied sparingly, as thick layers crack.

The following brief hints indicate the general circumstances in which different cements should be used:—

Fireclay and grog—where tightness and great strength are not essential.

High-temperature fireclay cement—for furnaces built of fireclay bricks where the temperatures are not excessive, or at higher temperatures in the absence of corrosive dust and slags.

Chrome-magnesia cements—for boilers using coal with fusible ash, for boilers at high ratings and for metallurgical furnaces.

Special refractory cements—for all special refractory bricks, *e.g*, magnesia, chrome, sillimanite, alumina, and silicon carbide bricks.

Tamped linings are sometimes made of the same materials as refractory concrete. For further information see p. 800.

General Properties.—The essential characteristics of a good refractory cement are:

(i) As nearly as possible, it should have the same total shrinkage as the work to which it is applied; as the latter is usually brickwork, the shrinkage of the cement must be low.

(ii) The coefficient of expansion or contraction should be equal to that of the bricks on which the cement is to be used.

(iii) The refractoriness should be ample; it should, preferably, be tested by the refractoriness-under-load test. Many cements have a low refractoriness because they contain too much added flux, or an insufficiently refractory non-plastic material.

(iv) A suitable consistency, which must be retained until used.

(v) Sufficient resistance to slag, flue-dust, and abrasion; this usually necessitates a low porosity.

(vi) Sufficient adhesiveness, so as to yield without loss of adhesion to changes in the brickwork.

(vii) Good working properties—some cements are too rough under the trowel. Good workability is best secured by careful grading of the non-plastic material.

(viii) A minimum reaction on the brickwork.

(ix) A long range of vitrification, so as to adhere strongly at a moderate temperature and yet become " fluid " whilst in use.

(x) The time required for setting should be suitable.

(xi) The cement should not be difficult to prepare for use (or if sold " ready for use " and allowed to dry, must mix easily with water). Some dry cements ball badly, or even set in lumps, and are then unsatisfactory. Some pasty cements are too stiff and too coarse.

(xii) The cement should be packed in convenient containers. For paste cements, the container must be air-tight after some material has been used. Some drums cannot be closed properly when once they have been opened.

In short, the mortar or cement should, when in use, have a composition and properties corresponding to the brickwork with which it is used; it should not offer less resistance to heat, corrosion or abrasion, or the joints will give way before the brickwork is affected. The cement should have ample strength at all temperatures at which it is used, but great strength at low or moderate temperatures should not be obtained by the sacrifice of too much refractoriness. The reversible expansion and contraction should be as similar as possible to those of the bricks, and the irreversible expansion or shrinkage must not be excessive.

As slags penetrate joints much more rapidly than bricks, it is important to make the joints as thin as possible, and to ensure this it is often advisable to use only bricks which have been ground accurately to shape.

The various materials should be skilfully selected and those of inferior quality should be avoided. The day is past when "rubbish" could be sold satisfactorily as "cement" or "compo."

The chief defects in refractory cements are:

(1) Insufficient refractoriness, usually due to inferior material or too much silicate of soda.
(2) Excessive shrinkage, often due to an excess of clay or water.
(3) Excessive expansion on continued use.
(4) Insufficient adhesion to the brickwork.
(5) Insufficient cohesion among the particles of cement.

Preparation.—It is customary to sell refractory mortars and cements in two forms: (*a*) as a *moist paste* ready for use, and (*b*) as a dry powder which requires to be mixed with water. It is advantageous to users to employ different forms of cement for different purposes, so that there is a commercial demand for the following:—

(i) *A moderately coarse, plastic cement for general use*, either for laying bricks or for coating brickwork. This should be an air-setting cement.

(ii) *A fine plastic cement* for pointing joints and repairing small defects, especially useful to builders for domestic repairs. It should resemble (i), but the aggregate should not contain any particles larger than $\frac{1}{32}$ inch. Some users prefer a still finer aggregate.

(iii) *A stiff paste*, which requires to be tamped or rammed into position. It is chiefly used for filling hollow spaces and making portions of wall-blocks, etc. It may be regarded as a *refractory plastic* (p. 746).

(iv) *A wash* or *slip* (see p. 741), which can be applied with a brush or spraying machine.

Each of these forms can be made from any of the classes of cement described on the preceding pages. It is largely a matter of convenience whether they are supplied ready for use or as dry cements.

To prepare a *dry powder* cement, the raw materials should be ground separately, weighed or measured in the desired proportions, and then mixed mechanically in the ball mill, or an edge-runner mill with solid pan. Some firms mix the materials in the desired proportions and then grind the mixture in an edge-runner mill with perforated pan, the mixing and grinding taking place simultaneously. There are obvious drawbacks to this method, though it is extensively used. The objections are largely overcome if a ball mill is used instead of an edge-runner mill. In fact, the most generally satisfactory method is to use a ball mill.

The mortar must be very finely ground—preferably in a dry state—as coarse particles do not bind sufficiently. The grains, mixed into a thin cream with water, should all pass through a No. 40 sieve if the best results are desired.

Too much dust (other than clay) should be avoided, and care should be taken that all the particles are not of the same size.

When *pastes* are to be produced, the action of light runners (as in a tempering mill) is usually considered to be advantageous, but the runners must not crush the aggregate. Their chief advantage is supposed to lie in their greater power of coating the non-plastic particles with plastic paste, but some modern mixers without runners appear to be equally satisfactory.

Whatever the method of preparation, no pains should be spared to secure the most thorough mixing.

The *user* of refractory mortar for laying bricks should be encouraged to convert it into a slip or cream and not into a soft paste. For coating the surface of brickwork, either a plastic cement should be used or a dry cement should be converted into a paste by adding water and, where practicable, using a mechanical mixer in preference to hand-mixing.

Making the Slip.—The mortar used for laying refractory bricks and blocks should not be in a paste like lime mortar, but should be in the form of a slip or cream. For patching, a paste may be employed, but this is too stiff for proper bricklaying.

Some firms boil the materials with water, being under the impression that this treatment reduces the shrinkage. Actually, it does not do so, and its chief advantage is in the uniformity of the mixed materials caused by making a very fluid slip previous to boiling.

If the mortar is to be mixed with water, the ground material (previously mixed as described above) is placed in a shallow box about 6 feet by 2 feet by 1 foot 6 inches, and water is added through a watering-can fitted with a rose having very fine holes. Sufficient water should be added to produce a rather thin paste. This paste should be allowed to stand a short time,[1] so that the water may penetrate it uniformly, after which a further quantity of water is added and the slip or slurry well mixed by stirring it with a wooden beater. The slip is passed through a No. 16 sieve before use; this assists the mixing and keeps out coarse particles. The most satisfactory fluidity is that at which the material can be poured readily from an iron spoon. A slurry as thick as porridge is not satisfactory, as it does not permit sufficiently thin joints to be made.

When in use, the mortar must be stirred repeatedly so as to prevent it settling, and any lumps must be rubbed out.

When the mortar contains tar, a similar fluidity is obtained by using hot tar and keeping it and the bricks hot whilst the mixture is being used.

Application.—In order that a furnace lining or other structure made of firebricks may prove satisfactory, it is of the greatest importance that the bricklayers shall do their work in a skilful manner. The methods of bonding the bricks are rather different from those used by ordinary architectural bricklayers and, as already explained, the jointing material is quite different from the mortar used for outside work.

Refractory mortars should be used only for forming the joints between the bricks; for this purpose they should be in the form of a slip (see *above*).

Refractory cements and refractory concrete are chiefly used for (i) making thick joints where these are essential, (ii) coating the brickwork and so protecting it, and (iii) filling hollows, fissures, and cracks and "making good" the damaged surface of the brickwork.

For *bricklaying*, the best method is for the bricklayer to pour a little fluid mortar on to the work previously laid and spread this evenly. He then

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[1] If Portland cement is present it will not permit of such treatment, but must be used at once.

either holds the new brick[1] upside down, pours slurry on it and inverts it, or he dips the brick into the slurry. If any additional mortar is required it is poured on with a large spoon, the flat trowel being unsuitable for refractory work. In all cases, the surface which will be placed on the brick below must be covered with the slurry. The brick is then laid in position and rubbed backwards and forwards so as to give it a " grip " on the mortar below. Finally, when it has been placed as accurately as possible, it is struck several times with a mallet so as to " drive it home." If a hammer is used instead of a mallet, a piece of wood should be interposed between the hammer and the brick, for if the former strikes directly on the bricks some of them will be broken.

The joints should be as thin as possible, as thick joints are a source of great weakness in high temperature work and offer too much weak surface to corrosive influences. For this reason, it is desirable to lay the bricks with as many stretchers as possible, though this must not be done to an extent which will diminish the strength of the brickwork below a reasonable limit. The precise number of headers and stretchers differs in each part of a kiln or furnace, and must be learned by experience: it cannot be reduced to a few simple rules, except the very general one just mentioned. Some kiln builders persist in laying the bricks in small arches exclusively as headers, with the idea that this gives a better key and a stronger arch. This may be true so long as the arch remains cool, but if it is to be subjected to the corrosive action of slags or flue-dust, any strength which may be gained in the key will be lost in the greater rapidity with which the larger area of jointing material is affected by the corrosion.

The greatest resistance to heat is obtained when arch and crown blocks are made specially to suit the radius to which they are to be worked, and though some builders avoid working with specially made bricks because of the cost, they will all admit, if questioned, that the purpose-made blocks give the best and most durable construction for all arched and domed work. Bricks and blocks which have to be cut, or the spaces between which have to be filled with cement, are never really satisfactory for kilns and furnace work, because, no matter how carefully the bricklayer may work or how tightly he may try to hammer the bricks into position, he cannot avoid the detrimental effects of shrinkage of the cement on the structure as a whole.

The thickness of joint to be aimed at is one not wider than $\frac{1}{16}$ inch, but, to get this, care is needed in laying as well as in the preparation of the mortar. If the bricks are very irregular in shape, it will be impossible to lay them to the best advantage.

Any wide parts of the joints—such as those due to broken bricks—should not be filled with an ordinary mortar, but with a mixture of crushed bricks and only sufficient clay to bind the particles together. The use of an ordinary fireclay mortar for this purpose is futile, as the clay shrinks too much and readily falls out of the joints. At the same time, the use of badly shaped or chipped bricks should be avoided, as no mere mixture of grog and clay can have the same resistance to flame or slag as that possessed by the bricks themselves.

Too much mortar should be avoided and, if more than 8 cwt. of the dry cement is used for each 1000 bricks, some endeavour should be made to reduce it, either by insisting on thinner joints or by providing purpose-made bricks or blocks. The usual allowance of 10 cwt. per 1000 bricks is excessive.

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[1] The custom of immersing the bricks in clean water before use should be avoided; it is quite unnecessary and unduly wets the bricks. If the cement slip is sufficiently thin, dipping the bricks in it is a far better method.

Thicker joints can be tolerated in the outer masonry, which must be more deformable than in the refractory part. Deformation there partially manifests itself by a compression of the joints and thus allows for expansion of the interior brickwork.

The use of thin, inside joints and thicker outside ones ensures resistance to the crushing stress of the refractory mass and a sufficient deformability of the brick casing. Yet, in spite of all precautions, ideal conditions are never completely realised. The pressure developed inside the masonry is not equal in all places and, on firing the furnace, this difference in pressure and resistance produces cracks on the exterior, especially in the brick joints, which are the weak places. The extent of the cracks produced on firing is not usually proportional to the degree of expansion. There are general movements in the mass (such as sliding and rotation) which increase the cracks. When a furnace is extinguished, the cracks do not close completely, and they become larger when the furnace is again fired.

To keep these cracks within certain limits and ensure stability of the furnace, iron bands or vertical iron pillars connected by means of tie-rods are used.

Refractory brickwork, if well laid, always has a dirty finish, as the mortar is squeezed out of the joints by the rubbing and striking, and it then trickles down over the surface of the bricks. For this reason, it is sometimes " washed over " with more of the mortar applied with a brush. This practice of coating the surface of the brickwork with mortar is objectionable. Such a coating is seldom durable and, in all cases, it is less refractory than the bricks if the latter are properly made. The proper way is to clean all mortar from the faces of the bricks and to point the joints with a refractory cement.

Before a freshly built refractory structure is used, or after it has been repaired extensively, it must be carefully heated. This process is known as " drying out," but the heating should be continued for some time after the water has been driven off, as the mortar requires to be burned before it reaches its maximum strength. In most cases, the temperature reached in this " drying out " should be as high as that when the structure is in use, as, unlike lime mortar, that used for furnaces, kilns, and fire-boxes does not become changed on exposure to air, but obtains its binding power from the heat to which it is subjected in use. It is essential to warm the masonry slowly and thoroughly, as the mortar as well as the bricks will be dislocated by a too sudden evaporation of the water.

A wise builder will only employ bricklayers who are used to furnaces when having such work done, as the ordinary bricklayer is rarely a success with them, owing to the great differences in the requirements of furnaces and ordinary brickwork. Men who have had a good practical acquaintance with the subject will also be better able to allow the necessary corrections for expansion and movement with the changes in temperature which the brickwork has to undergo. These allowances do not admit of any general formula being used whereby they may be calculated beforehand, so much must be left to the man in charge.

Tests of various cements and mortars should be carried out under conditions similar to those under which the materials will be used. An excellent method is to cement two bricks together with the material to be tested. Merely to test a sample of cement in the mass is of little value, and has been shown by Blauvelt to be seriously misleading in some instances. (See also under Specifications, p. 809.)

Patching and coating are best done with a refractory cement of soft or stiff consistency, according to the work, and of similar aggregate to the bricks.

The patching of defective parts of retorts, settings, and furnaces is unavoidable if they are to be used for the longest possible time. Such patchwork is seldom satisfactory, and is often so badly executed that it is almost useless. With care, on the contrary, a well-made patch often adds greatly to the length of time a retort setting or furnace may be used, and such a patch is then well worth the time, labour, and materials expended upon it.

Patches on refractory materials should, as far as possible, be made of the same materials as those to which they are applied. Thus, silica brickwork should usually be patched with a material rich in calcined silica, whilst a structure made of fireclay is preferably patched with a cement in which fireclay is the chief constituent. A little coke is sometimes added, and some firms prefer also to add a little sand or crushed silica rock.

As fireclay shrinks greatly when heated, it is usually necessary to mix it with a considerable proportion of non-plastic material, the most suitable being grog made by reducing fireclay bricks to a coarse powder. The proportions of grog and clay are best found by trial, as so much depends on the angularity of the grains, their sizes, and on the binding power of the clay.

It is usual to employ a large proportion of fireclay in patching, but in the author's experience this has been much less satisfactory than the use of a much smaller proportion of a more highly plastic clay, such as a rich ball clay. A very small proportion of ball clay will be equally as effective—if properly used—as a large proportion of fireclay.

For patching silica brickwork, a mixture of crushed silica bricks and ball clay is excellent, but if a very lean mixture will suffice, it is often more convenient to use a natural mixture such as ganister, for in no artificial mixture are the non-plastic grains so uniformly coated as in some natural ones. At the same time, a well-made artificial mixture is quite satisfactory, and is more reliable than some of the natural mixtures, as the latter sometimes vary greatly in composition and properties and their quality is more difficult to control.

An effective patch must adhere well to the surface to which it is applied, and must remain adherent as long as may be required. Some patching materials adhere well when cold, but tend to shrink or expand and then to fall away when heated; other materials adhere well after heating, but are liable to fall away during the first heating. The former patching materials may usually be improved by adding grog made of crushed fireclay bricks, or by the addition of water-glass or Portland cement, the grog being a diluent to reduce the shrinkage or expansion of the cement, whilst the water-glass is, in itself, an excellent binding agent which hardens on exposure and still more rapidly when warmed. The Portland cement sets even more rapidly than the water-glass, and for some purposes is preferable to the latter, though it has a more serious effect on the heat-resistance of the brickwork or retorts at high temperatures. Speaking broadly, Portland cement is preferable when very great strength is required in the cold and very quickly after the application of the patch, whilst water-glass is preferable when the cement is to be applied to a warm surface or where a quick-setting cement is not essential.

The purposes for which patches are required are so numerous that no single cement will be equally useful for all, though a carefully prepared mixture of grog and ball clay or fireclay will serve most purposes. Suitable cements for each kind of work are now available, and it is worth while taking pains to select the one which is best for the purpose.

The surface to which the patch is to be applied should be thoroughly cleansed and roughened, a " new " surface being exposed, as the cement will adhere better to this than to a long exposed surface. If time permits, a little of the cement—preferably diluted with half its volume of water—should be well rubbed into the exposed surface with a hand brush. This will form a well-adherent film of cement, to which the remainder of the cement can be applied with better effect than if this preliminary application were omitted. Where a patch is very large, it is often better to fill it with broken firebricks or the like so as to reduce the amount of cement required, for all cements tend to shrink when heated and, therefore, should not be used in large masses. If possible, the cement should be compressed by tapping it with a mallet or other suitable tool so as to squeeze out all surplus jointing material, which should then be removed.

Care should be taken not to heat the patchwork too rapidly, or its adhesion will be lessened and the patchwork may fall away. The chief risk is at temperatures between 80° F. and 250° F., and again between 950° F. and 1200° F., but if the rate of heating between these two ranges of temperature is not too rapid, a suitable cement should make a patch which is quite durable and as satisfactory as any patch can be.

Hot Patching.—The most difficult conditions for making a good patch are when the part to be repaired is hot and not readily accessible.

With hot brickwork, it is difficult to secure adhesion, as the application of a wet material causes the evolution of steam between the brickwork and the applied cement. The use of a dry cement applied through a blast of gas and air (Eng. Pat. 402,203—1932) appears to overcome this difficulty in those parts of furnaces where it can be used. A cement with an organic binder is sometimes useful, but the patch tends to fall off when the temporary binder has burned away and before sufficient vitrification has occurred. Another method of assisting adhesion is to use a stiff cement which contains a flux which becomes effective at a low temperature. A mixture of grog with borax, or with sodium silicate, is often satisfactory, but in some instances borax cements have not proved durable, and some silicate cements have behaved erratically. The latter may be due to an unsuitable form of sodium silicate; the least troublesome corresponds to the formula $2Na_2O.5SiO_2$. Cements of the No. 3 class (p. 727) are also used with complete satisfaction for some hot patches.

H. E. Pardoe [1] has suggested a mixture of 56 parts of fine silica (200-mesh), 37 parts of calcined bauxite (10-mesh), 3 parts of flint glass (100-mesh), 2 parts of vegetable glue, and 1·5 parts of lime.

The cement should be selected according to the conditions to which it will be subject. A highly refractory cement is not always the best; it may be less effective than a cement of lower refractoriness which adheres better to the brickwork. For extremely trying conditions in hot patching, Clews, Booth and Green have found chrome cements to be specially suitable, but several proprietary cements give satisfactory results.

Cements and concrete made with *ciment fondu* or Portland cement are not suitable for hot patching, as they must be kept moist for 24 hours after being applied. Patches and coatings of refractory cement may be applied by means of a trowel, a brush, a spraying device (which requires a semi-fluid material), or a cement gun (which uses a dry material).

The *cement gun* [2] consists of a container for the dry material and an air-compressor which forces the dry material through the nozzle, in which water under pressure is mixed with the stream of dry material, which is then carried

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[1] *Trans. Cer. Soc.*, 1930, **29**, 87.

[2] Made by the Cement Gun Co., Ltd., London.

forward and deposited with great force on the surface to be covered. At first some of the applied material rebounds from the surface and falls away, but gradually a layer is built up to any desired thickness.

The Cement Gun Co. recommends a mixture of grog 3 parts and fireclay 1 part, or ganister 3 parts and fireclay 1 part, for general use, but for special purposes other mixtures, including most of the dry refractory cements previously mentioned, should be considered.

The chief advantage of using a cement gun, of the type described, is that the monolithic layer is much denser and harder and it adheres much more strongly than when the same mixture is applied in any other manner.

PLASTIC REFRACTORIES.

The terms *plastic refractories* and *refractory plastics* are used for refractory pastes which can be used for forming tamped monolithic linings and for repairing hollows in the interior of furnaces, retorts, etc. They are really included under refractory cements (p. 723), as the same compositions are used, though the consistency may be varied to suit local requirements. A plastic refractory is rather stiffer than most refractory cements.

Much attention has recently been attracted to *refractory concrete*, which is made of:

(i) A *refractory aggregate*, such as grog, calcined silica rock,[1] dead-burned magnesite or dolomite, chromite, sillimanite, silicon carbide, etc. Old firebricks may also be crushed, screened, and used as an aggregate.

(ii) A *hydraulic cement*, such as Portland cement or, preferably, *ciment fondu*. It resembles, in many respects, refractory cements of class 4 (p. 729).

Refractory concrete has the great advantage of setting and hardening quickly, so that it can be used for building up structures, as well as for patching or coating brickwork. There is little drying shrinkage and little spalling, and the concrete can be heated up fairly rapidly without much risk of disintegration.

Coarse aggregate is used for large masses and thick coatings; it may consist of pieces from ⅕ to 1 inch in diameter. Fine aggregate is used for smaller masses and thinner coatings; it usually consists of particles less than ⅛ inch in diameter, but should not contain more than 15 per cent. of material fine enough to pass through a 100-mesh sieve. In large masses, and for thick coatings, a mixture of both coarse and fine aggregate should be used. For the hydraulic cement, it is better to use *ciment fondu*, for the reason stated on p. 730, though Portland cement can be used satisfactorily in some cases where the temperature does not exceed about 950° to 1000° C.

The normal *proportions* of aggregate and *ciment fondu* are 5 parts of aggregate to 1 of the cement (by volume), but either a smaller (2½ : 1 to 4 : 1), or a larger (6 : 1) proportion of aggregate may be used.

For large articles and "concrete," it is best to use two grades of aggregate:

Coarse aggregate (¾ inch–⅛ inch) . . .	3 vols.
Fine aggregate (⅛ inch and below) . . .	2 ,,
Ciment fondu	1 vol.

For coating brickwork, the proportions should, usually, be four volumes of fine aggregate to each volume of *ciment fondu*.

Great care is necessary not to use too large a proportion of binder or cement

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[1] Raw silica, ganister, or sand should not be used as aggregate, as it expands excessively when heated.

with the aggregate, or the shrinkage will be excessive and will cause cracking. The " leanest " mixture consistent with safety is usually the best. All the customary precautions when joining new to old concrete are specially necessary when this material is used in furnace-construction and repairs.

Before mixing, the aggregate should be soaked in water; the *ciment fondu* is then added and mixed for about 20 minutes. The greatest care should be taken not to mix Portland cement with *ciment fondu,* as each destroys the other's setting and hardening properties. Too much water must be avoided, as a sloppy concrete loses part of the cement.

Refractory concrete hardens without heat, but when it reaches a temperature of about 400° C. the hydraulic cement begins to decompose, so that the whole mass is weak from 400° to 1100° C., *i.e.* until sufficient vitrification occurs to produce a stronger mass. Above this temperature, refractory concrete regains strength.

Properties.—Refractory concrete made with a suitable aggregate and *ciment fondu* has the following properties:—

(i) It can be made into any desired shape or applied as a coating of any desired thickness.

(ii) The highest safe working temperature is 1300° C., but with chrome or chrome-magnesia aggregate it can be used up to 1600° C.

(iii) It has no appreciable shrinkage during drying or when in use. After-contraction at 1350° C.=0·75 per cent.

(iv) It can be raised to furnace temperature 24 hours after being placed in position.

(v) It is not sensitive to sudden changes in temperature.

(vi) It is essential that the concrete should be kept moist for 24 hours after being made, in order that the hydraulic power may be properly developed. Failure to " cure " the concrete, in this way, can lead to serious loss. For the same reason, it cannot be used for " hot patching " (p. 745).

The refractoriness-under-load of a concrete containing 5 vols. of grog and 1 vol. of *ciment fondu* is 1240° to 1400° C.

The thermal conductivity is rather less than that of fireclay bricks.

Furnace Paints and Washes.

Furnace paints and washes are very similar to refractory cements and are made of the same ingredients, but with a large proportion of water, so as to form either a very soft paste or a slip or cream. Many furnace paints and washes are made by adding water to a (purchased) refractory cement, but suitable washes of similar composition can be purchased ready for use.

Furnace paints and washes are chiefly used to protect the surface of refractory brickwork from flashes of flame. They usually form so thin a coating as to be almost useless, but are popularly credited with being of great value. Where better protection is required, a thicker coating of refractory cement in the form of a paste should be applied.

Furnace paints and washes may be applied by means of a brush or a spraying device (" gun," pp. 654 and 745) operated by compressed air; several coatings are sometimes used.

A thin refractory coating may be produced by blowing a mixture of metallic aluminium powder and refractory brick-dust through a blast of gas with air or oxygen. The flame heats the material to be coated and also the aluminium and forms an adherent coating. Other metals may be used (see Eng. Pat. 402,203—1932).

Paints are also used in foundry work to protect the moulds from being damaged by the metal and to ensure a good surface on the latter, so that the casting, when sufficiently cool, can be easily removed. These paints must be free from dust and be homogeneous. They are prepared by suspending the mixed materials in water and applying the resultant slurry by means of a brush.

They are usually composed of grog, old crucibles, graphite, clay, and sand, but vary greatly in composition. For medium-sized castings a mixture of graphite, fireclay, and treacle is excellent.

CHAPTER XVIII.

THE SELECTION AND APPLICATION OF REFRACTORY MATERIALS.

IN the previous chapters the uses of various kinds of refractory materials have been mentioned; in the following pages the kinds of material best suited for particular purposes are described. To treat this branch of the subject exhaustively would require several volumes the size of the present one, but it is hoped that the information here given will be sufficient to show the reader the leading characteristics required in refractory materials to be used for any particular purpose, to enable him to make a reasonably good selection and to indicate the lines on which a more detailed study of the subject may most profitably be pursued.

The materials used in the construction of furnaces are divisible into two classes: (i) ordinary, and (ii) refractory materials. The former are used principally for casing, filling, walls, pillars, and other supporting parts of the structure, and include ordinary red or yellow bricks, iron, slate, granite, and most building stones, whilst the latter are reserved for parts immediately in contact with the fuel and flame, such as the lining of the fireplace, the arches, roof, and flues, the lower part, if not the whole, of the chimney lining, the whole of the internal walls of kilns, and most of the brickwork in furnaces.

The destruction of bricks in furnaces is usually due to one or more of the following causes:—

(*a*) *Crumbling*—caused by the bricks being too weak (or excessively porous) at a high temperature.

(*b*) *Shattering*—due to the material being too weak, or else to its being too fine and overburned, so that it cannot resist sudden changes in temperature.

(*c*) *Abrasion*—especially that effected by the movement of the contents of the furnace. In shaft furnaces, this includes the damage wrought by the descending charge. The abrasion of the exposed bricks by flue-dust, accompanied by vitrification, will wear away a brick, however refractory it may be; this is especially the case with bricks used for flues and furnaces, as the flue-dust and ashes coming into contact with the bricks vitrify the exposed portions and form a coating of viscid slag, which gradually corrodes the surface and, in time, destroys the brickwork. This is particularly noticeable in blast furnaces at the point where the impact of the blast occurs.

(*d*) *Vitrification* or *partial fusion*—caused by excessive heating or by the combination of ash or other basic matter with the brick material and so producing a compound of lower fusing-point than the brick alone. On account of this, the brick gradually vitrifies and, under the pressure of the superimposed structure, is slowly squeezed out of shape and has to be replaced. No matter how completely a brick has been burned, constant exposure to very high temperature will cause it to shrink still further; and this will eventually cause the displacement of the mass of which it forms a part, necessitating replacement or repair.

(*e*) *Internal strains*—due to the alternate heating and cooling of the furnace and to any chemical or physical changes in the material which may result on prolonged heating. Among the most important of these are the strains due to shrinkage or expansion of the refractory material when in use. If the refractory material happens to be a good conductor of heat, these are not serious, unless one face is rapidly heated and the distortion produced exceeds the tenacity of the material. The best way is to avoid rapid temperature changes whenever possible and to burn the refractory material at a temperature well above that at which the chief inversion or the principal volume change should take place, and hold it at that temperature long enough for inversion to be completed as far as possible. The " spalling " of magnesia bricks which sometimes occurs has been avoided in this manner, and the excessive expansion of silica bricks would be avoided if the manufacturer could ensure the completion of the quartz-tridymite inversion during burning.

(*f*) *Corrosion* by flue-dust, slag, or other substances having a chemical action on the refractory material. Such corrosion must be distinguished from what is sometimes termed " mechanical corrosion," which is described in section (*c*) under *Abrasion*. True chemical corrosion in the interior of a refractory brick is due to the improper chemical composition of the materials used in the manufacture of the article, whilst external corrosion is due to incompatibility between the refractory material and the gases and other substances with which it comes into contact. External corrosion occurs more rapidly when the refractory material contains a flux of the same character as the external corrosive agent—as lime and alkalies present in the firebricks which are in contact with slag or glass. As the jointing materials used are generally richer in fluxes than the bricks and blocks, the joints in the brickwork of a furnace are the lines of greatest weakness and should, therefore, be as small as possible. In some cases, the difficulty of having too many corrodible joints is avoided by using blocks measuring 18 to 36 inches by 10 to 15 inches by 5 to 8 inches instead of bricks of the standard size. One such block will be equal to eight to thirty-six standard bricks. The chief disadvantages of large blocks are the increased difficulty of manufacture—the loss on drying and burning being much greater than with the corresponding number of bricks of standard size—and the much greater weight to be lifted at a time.

Which (if any) of the foregoing causes operates in any given case can only be ascertained by a study of the furnace itself. Hence, the more general information should be considered in connection with that based on actual experience of a particular furnace or kiln and not merely on several of a type.

Thus, for the construction of a *boiler-setting*, the resistance of the firebricks to the corrosive or abrasive action of flue-dust is much more important than an unduly high degree of resistance to heat, so that for this purpose a moderately dense brick with a close surface and of very accurate shape is much more valuable than an open-textured, soft brick with a far higher melting-point. The latter would be rapidly worn away by the action of the flue-dust and its great resistance to heat would be largely wasted.

Hence, one of the important points in brick manufacture is to obtain bricks which will be both sufficiently refractory and able to stand wear and tear, for, in most cases, the refractoriness diminishes as the mechanical strength increases, and neglecting to use the right kind of bricks for the service required is one of the chief causes of the failure of firebrick work. For this reason, it is not always necessary to pay a high price, as much cheaper bricks will often give better service if rightly selected. The price charged for firebricks is no criterion of their value for any particular purpose.

Unless intelligence is employed in the application and use of firebricks, a really excellent brick is liable to be unjustly condemned; this has not infrequently been the case. Hence, a brick which has given the best service and is recommended in the highest terms by one user may, when used by another, prove to be utterly worthless. The difference is in the conditions under which the brick is used, and firms should, when ordering, state the purpose for which the bricks are required, so that the makers may send those suitable for that purpose. A firebrick that is first-class in a blast furnace may not give good results in a heating furnace, and bricks which are the very best for a hearth and bosh are often the very worst for a tunnel head. In short, a clay which makes a high-class brick for one purpose may not be at all suited for another, although in this respect much depends upon the skill of the manufacturer and of the user.

It is necessary, then, before deciding upon a suitable firebrick for any particular purpose, to examine the conditions which are likely to be prevalent and to subject them to inquiry on lines such as the following:—(*a*) What is the highest temperature to which the brick will be exposed (excessive or only moderate), and will it be constant or fluctuating? (*b*) Will the material come into direct contact with any flame, and will the latter be of an "oxidising" or "reducing" character? (*c*) Is mechanical strength required? (*d*) Is heat to be conducted or retained? (*e*) Is the brick expected to withstand sudden and repeated changes in temperature? (*f*) Will the brick come into contact with fluid slags or glass, or with flue-dust, lime, cement, or other fluxes? (*g*) Must the brick resist blows, shocks, and other unavoidable strains? (*h*) What is the nature of the fuel used and is it fed by hand or mechanically? (*i*) Is the electrical conductivity important?

To meet (*a*) refractoriness is of much importance, but, in most cases, other factors deserve even greater attention. For (*b*) and (*c*) the texture of the surface of the brick must be right or the brick will not be durable, no matter how great its refractoriness. If mechanical strength is needed, the brick cannot be as refractory as otherwise, for great strength is dependent on the presence of a large amount of bond, which is necessarily less refractory than the particles to be bound together. For (*e*) a lean, coarse, and porous material should be used, whilst for (*f*) a fat, close material is required, *i.e.* exactly opposite to that for (*e*), and for (*g*) a hard-burned material which has not been heated more than once is preferable; broken bricks and other refractory articles should not be used as grog in this case. The mass should not be either too lean or too fine-grained.

Consideration of the above points will show that there is some difficulty in deciding upon the correct description of the material for use in the ordinary type of industrial furnace, though most of the requirements are satisfied by using an open-grained, porous material. Still greater difficulty arises in dealing with furnaces in which fluxes are brought into contact with the firebricks, and in these the material must be close-grained, even if this is accompanied by the loss of some heat resistance.

Where great resistance to fluxes (flue-dust, lime, and other bases) is required the refractoriness of the brick is second in importance to the closeness of texture. Under such conditions, a porous, highly refractory brick will be far less durable than a dense brick of much lower fusing-point. The fluxes act less rapidly on a comparatively smooth, dense surface than on a more porous one, so that the "life" of the former brick will be longer than the latter, notwithstanding the fact that its actual heat resistance may be lower. For this reason, many fireclays which are of No. 2 quality as regards heat resistance are preferable for use in some furnaces and for flue work generally.

In some heating appliances, the *draught* and the *atmosphere* to which the refractory material is exposed have a far greater influence on the durability of the latter than is generally supposed. Unless properly managed, such furnaces may cause firebricks to be destroyed in a few weeks, whereas under proper conditions of draught they would last almost as many years. This is a matter of which firebrick manufacturers have no special knowledge and most builders and users of furnaces are equally ignorant. It is, in fact, one which can only be properly investigated by a specialist in refractory materials.

Closely allied to the foregoing is the shape, size, and construction of the *combustion chamber* or fireplace; if any of these is unsuitable it may be impossible to provide durable bricks, as the conditions may be such that no firebricks can withstand them.

The *fuel* used in a furnace or kiln and the method of stoking may also have an adverse influence on the refractory materials used. Thus, in furnaces where bituminous coal is used, hard dense bricks of great refractoriness are requisite, especially along the clinker line.

In furnaces in which a solid fuel is used or in water-gas producers having refractory linings, a contingency which has to be guarded against is the fluxing action which may be set up by the alkalies in the fuel. The same action may be caused by the waste gases circulating in coke-fired furnaces; these gases are highly charged with dust which contains a large proportion of iron, and this, in conjunction with intense heat—particularly if the atmosphere is "reducing"—may cause a "running" of the material.

The fact that very porous fireclay bricks can, when heated, decompose carbon monoxide, with production of free carbon, is often overlooked, but it is extremely important in selecting firebricks for lining gas-producers. The same action occurs when fireclay bricks are heated in a reducing atmosphere and it is, therefore, necessary to use bricks with a dense surface if the action of carbon monoxide is to be reduced to a minimum.

In endeavouring to determine what is the most suitable material for the purpose, it must be remembered that a low initial cost does not necessarily mean a really cheaper lining, for, with an unsuitable material, the cost of repairs will more than counterbalance the saving effected in the cost of construction. Added to this is the greater time the furnace is out of use and the consequent loss, due to the capital thus locked up and to the disturbance of trade, which is often as much as, or even more than, the actual cost of the repairs.

The difficulty of satisfactory selection is increased by the great differences in the conditions to which refractory materials are subjected even in similar types of furnaces or kilns. The differences in the fuel used and apparently slight variations in the constructional details and methods of working, result in bricks proving highly satisfactory in one works, but failures at another using boilers, ovens, or kilns of the same type. Indeed, different parts of a furnace usually require to be built of entirely different kinds of firebrick.

In the following pages, it is only possible to give the *general* characteristics required in each of the appliances mentioned; a complete study of the details can only be applied satisfactorily to one particular plant under observation, and would, therefore, be useless to others. Such a study should obviously be undertaken by an expert adviser on refractory materials, and it cannot be so effectively carried out by anyone else. Much may be done if the purchaser is an experienced engineer who has devoted a good deal of attention to the subject and works in close collaboration with an exceptionally able brick manufacturer, but their united efforts will be less effective than those of a fully qualified and wholly independent expert adviser aided by a competent staff.

Air Furnaces is an old name for reverberatory furnaces (p. 789).

Air Stoves are used for heating a supply of air for blast furnaces, and other furnaces where the combustion of the fuel is aided by hot air; they are also used for heating air required for drying purposes. Air stoves are usually recuperators or regenerators (see p. 785), the choice depending on whether the air must be kept free from products of combustion or not. Illustrations of air stoves for use in connection with blast furnaces are shown in fig. 170.

Aluminium Furnaces in which the metal is obtained by reduction are generally lined with carbon; petroleum coke was formerly used, but now picked anthracite and specially prepared coke from oil-floated bituminous coals are used. Furnaces for melting aluminium are usually of the reverberatory type with the hearth composed of fireclay bricks. The bricks when heated to 800° C. to 900° C. must be resistant to the corrosive action of molten aluminium, and strong enough to withstand the impact of cold pigs of metal thrown into the furnace. Linings made of rammed ganister are sometimes used in tilting, or rotating and tilting furnaces for melting aluminium, but for electric furnaces of these types the linings are usually made of fireclay bricks.

Aluminium metal and its alloys are usually melted in electric furnaces, and as the temperature is not high they make no special demands on the refractory materials. Alternatively, they may be melted in cast-iron "pots" or in plumbago crucibles. The aluminium must not absorb silicon or metallic iron in quantities sufficient to spoil it, as the refining of aluminium and its alloys is unremunerative.

Some aluminium alloys cannot be melted in contact with iron; in such a case, either a plumbago crucible or a furnace having a hearth lined with magnesia bricks is used.

Annealing Furnaces.—As the temperatures employed in annealing furnaces vary from only 800° C. to 1500° C., or possibly a little higher, second quality bricks may be used throughout, except in furnaces of great width and where the flame has to travel a considerable distance. It is generally necessary to use first-class quality bricks in the fire-boxes of coal-fired annealing furnaces on account of the higher temperatures necessary to carry the heat across the furnace.

The best practice is to build the bottom of these furnaces with tiles 12 inches wide, 2 to 5 inches thick, and varying in length from 12 inches to 18 inches. These tiles are made tough and dense so that they will stand the wear and abrasion of charging the furnace, though there are advantages in making them porous with a dense upper surface. The porous body withstands changes in temperature and the dense surface resists abrasion. As each of these blocks covers a larger area than a firebrick, they afford a more even surface and correspondingly reduce the number of joints in the brickwork.

The use of insulating bricks between the lining and the casing and foundations of the furnaces effects a notable saving in fuel. If the castings are stacked on a carriage or bogey, the top of this should be covered with dense, hard-burned fireclay bricks.

Antimony Furnaces are of two kinds; for roasting antimony ores, good fireclay bricks fulfil all ordinary requirements; for reducing the oxidised material to regulus, on the contrary, a material highly resistant to corrosive slags is needed; the best material is chromite bricks, but, where these cannot be used, fireclay bricks with at least 33 per cent. of alumina may be employed.

Arches in kilns and furnaces should be built of porous bricks with a coarse grain, as these are more " elastic " than those of closer texture. The bricks should be under- rather than over-burned, yet they must not shrink when in use. Silica bricks are often suitable, as they tend to expand rather than contract (Chapter III.).[1] Under some conditions, an open brick is not suitable for arches, *e.g.* with anthracite coal and blast or forced draught; here the physical structure of the brick should be dense and hard to withstand the cutting action of the rapidly moving combustion gases and the corrosive dust they contain.

Whenever possible, bricks used for arches should be made specially for the purpose. Bricks which have been cut or rubbed to shape are seldom satisfactory. The pressure of the superincumbent brickwork has an important influence on the durability of arch bricks.

Blast furnaces (fig. 167) are used for obtaining iron or other metals by heating their ores in contact with coal or coke. The fuel combines with the oxygen in the air, forming carbon monoxide gas, which in turn combines with the oxygen in the ore, setting the metal free. The temperature developed inside the furnace is sufficient to melt the metal and to fuse the impurities into a molten slag. To produce the necessary heat, a blast of hot air is blown into the lower part of the furnace through tuyères, this air being heated regeneratively in *air furnaces* or *stoves* (fig. 170).

The chief requisites in bricks for blast furnaces are—

(*a*) *Resistance to the abrasion* of the coke and ore descending through the furnace. This abrasion is the more serious as refractory materials tend to become softer when hot. Hard-burned bricks of close texture are the most suitable for resisting abrasion. The bricks near the top of such furnaces are chiefly abraded by fresh charges of ore and fuel, and the disintegration due to abrasion is increased by the formation of a friable scar and by careless charging. Differential movements of the charge also tend to damage the bricks and open up cracks and joints into which corrosive slags and vapours may penetrate.

(*b*) *Resistance to the chemical action* of the contents of the furnace, particularly soluble salts, alkalies, lime compounds (from both ore and coke), carbon, and reducing gases. This action is highly complex, and to avoid it the furnace lining must be as neutral or basic as possible. Hence, hard-burned grog bricks, or preferably magnesia bricks, should be used, though the latter are usually regarded as far too costly.

The chemical reactions which occur in the bricks in a blast furnace are of six main types:

(i) Combination of bases and alkalies (slag and coke-ash) with the clay or silica in the bricks, resulting in the formation of fusible slags and the destruction of the bricks. This action is most extensive with porous bricks rich in free silica, but does not occur with magnesia bricks.

(ii) The deposition of carbon on bricks in blast furnaces is due to: (i) the action of carbon dioxide on iron oxide and the removal of oxygen from the iron producing metallic iron and carbon; and (ii) the catalytic splitting up

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[1] It is not generally realised that ordinary firebricks will usually be found to contract on heating, whereas highly siliceous bricks of the Dinas type expand. These contrary properties have been turned to useful account in some of the latest types of furnaces, and by employing both kinds simultaneously the contraction of the one is counteracted by the expansion of the other, with the result that little or no displacement occurs.

of carbon monoxide into carbon and carbon dioxide. The most favourable conditions for carbon deposition are (see p. 353): (1) a temperature above 300° C., (2) a rapid flow of carbon monoxide, (3) a high percentage of carbon, and (4) the presence of metallic iron in a spongy form, as "spots" in the bricks. The deposition of carbon occurs chiefly with porous fireclay bricks and causes the bricks to disintegrate by flaking. With close-surfaced, hard-burned bricks it is inappreciable.

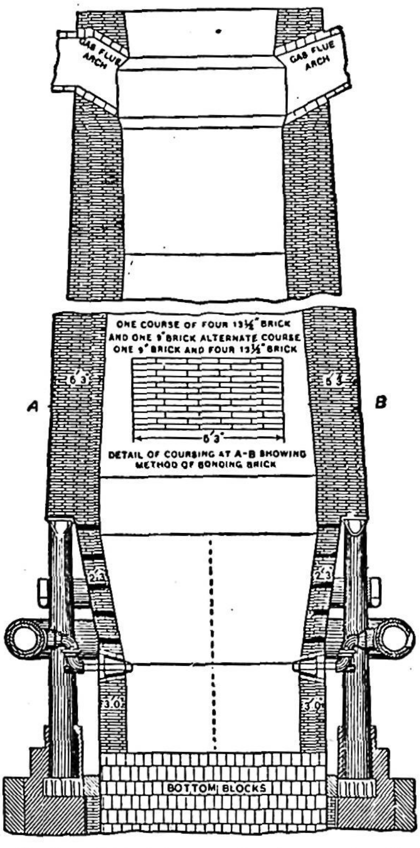

Fig. 167.—Section of blast furnace showing construction of lining.

(iii) Channelling, caused by the blast making its way up against the walls of the furnace instead of through the mass. This blast is charged with particles of coke, ore, and limestone, and acts like a sand blast in cutting the bricks. Its action is least with close-textured, hard-burned bricks.

(iv) The destruction of the bond in the bricks by the reducing action of the furnace gases, whereby the bricks are made friable.

(v) The deterioration of the bricks by the action of dust, especially when charging. This may be prevented to some extent by suppressing the dust before it reaches the regenerators, and possibly by using neutral or basic bricks made of bauxite, limestone, dolomite, or magnesian limestone.

(vi) Volatile metals, such as zinc and lead, and volatile salts of sodium, potassium, and ammonium have a "strongly corrosive action and require a dense brick to resist it."

(c) *Refractoriness* sufficient for the bricks to withstand the highest temperatures reached. This does not usually offer serious difficulty. Where bricks do not appear to be refractory enough, the fault is usually due to chemical or abrasive action and not to deficiency in true refractoriness.

(d) *Insensitiveness to Sudden Changes in Temperature.*—This requires porous bricks of moderately coarse grain and is in direct opposition to the characteristics which prevent chemical action or abrasion. Hence, a compromise must usually be effected either by (i) keeping the temperature uniform inside the furnace and taking great care to heat and cool it slowly, or (ii) by sacrificing some amount of porosity to gain resistance to abrasion and corrosion.

The refractory parts of blast furnaces frequently suffer from unsuitable treatment by the furnace-men, especially with regard to irregular working (often due to filling the furnace unsuitably), too rapid heating, forcing the furnace to work above its normal output, etc. No bricks can be made which will certainly be durable under such unfavourable conditions as may be produced by incompetency or carelessness in working a furnace.

The reactions which may occur in various parts of furnaces are so different that one kind of brick cannot be used throughout if the best results are to be obtained. The following considerations are, therefore, important:—

Hearth and bosh bricks should preferably be of a siliceous character and must have a close texture, be tough, and burned very hard, so that they resist disintegration by the reducing action of the blast-furnace gases at a high temperature and pressure. It is essential that they should be of the highest possible refractoriness, as well as resistant to the scouring action of slags and to great pressure.

There is an increasing use of highly aluminous bricks in the hearth and bosh, but care should be taken to ensure that the alumina and silica are in combination; this may not be the case if the bricks are made of fireclay and bauxite and have not been fired at 1500° C. or above. Fireclay bricks are very largely used with complete satisfaction in many blast furnaces.

Various means are used in up-to-date furnaces to protect the bosh walls and the crucible. Cooling plates made of copper may be used, but the rows ought not to be placed too far apart or the furnace may be continually hanging or slipping. This is due to the formation of ridges of a deposit consisting of carbon, silica, lime, etc., and if the rows of plates are too far apart, these ridges arrest the uniform descent of the charge. Spiral iron bands are sometimes riveted round the bosh shell so as to form a series of gradually sloping troughs through which the water flows. The bosh is lined to a thickness of about 12 inches; this brickwork is soon eaten away until the cooling action of the water is felt, when a carbonaceous deposit takes place and forms a protective coating.

The use of carbon bricks for lining has not become at all general in this country, although they have been tried in Germany, with good results; but as they are more expensive to produce than firebricks, their extra cost, in comparison with the benefit derived, may not warrant the change.

The hearth is gradually acted upon by the metal and slowly passes away with the slag, leaving a deep hole which remains filled with metal. When the furnace cools, this metal forms a *bear*, *old horse*, or *sow*, and may weigh over 100 tons. The lateral pressure of this metal on the brickwork of the furnace is sometimes fraught with serious consequences, as, being a good conductor of heat, it helps to melt the deposit or to impart carbon to it, and so lower its melting-point that it will be rendered liquid again by the molten metal in the hearth of the furnace.

Inwall Bricks.—The wearing away of the lining is most pronounced in the inwall above the bosh, so that bricks for the inwall should be exceedingly hard and dense, but they may be slightly less refractory than hearth and bosh bricks. Bricks made by the stiff-plastic process have proved exceedingly satisfactory, as they resist corrosion and abrasion well, though highly aluminous bricks are preferable for the lining of the shaft. Fireclay bricks containing 37 per cent. of alumina are usually satisfactory if they are of close texture, accurate in shape, and laid with the thinnest possible joints.

In the smelting of manganese ores for the manufacture of ferro-manganese and spiegeleisen, the brickwork in the upper zones of the furnace is very liable to be readily attacked if it is high in silica. A ferro-furnace tends to work with a hot throat. Manganese monoxide has a much greater affinity for silica than iron monoxide, and so readily acts on it to form silicate of manganese. In any blast furnace it seems advisable to use bricks having a high content of alumina where they come in contact with unreduced metallic oxides.

The nature of the materials to be smelted influences the life of the lining quite as much as the quality of the bricks used in its construction.

The *top bricks* must be harder than those for the hearth, bosh, and inwall. They must also be tough and of the greatest possible density. They are mainly required to resist abrasion, soot, and changes in temperature.

Piping bricks are often bought without regard to quality and then prove unsatisfactory. The requisite properties are a close interior surface, with a porous backing and sufficient refractoriness to resist the highest temperatures attained. These are similar characteristics to those of gas retorts and may be obtained by the same methods (Chapter XIV.).

Bricks to be used in blast furnaces must be accurate in shape and laid with the thinnest possible joints so as to reduce their liability to disintegration.

The size of bricks for blast furnace linings varies between 1 foot 3 inches to 3 feet long, 12 inches wide, and 4 to 4½ inches thick. In some cases, blocks or lumps 18 inches by 30 inches are used.

In short, fireclay bricks with 30 per cent. or more alumina, hard-burned, of close texture and accurate shape, so that they can be laid with thin joints, can be used throughout most blast furnaces. Bricks richer in alumina than those made from fireclay alone are preferable in the hearth and bosh and in the lower part of the stack, but they are not essential. Machine-pressed bricks are usually to be preferred, as they can be laid with the thinnest joints. Some users insist on the brick being ground accurately to size and shape; when this is done, care should be taken not to grind the *face* of the bricks. If the bricks near the top of the furnace are coated with a refractory cement and this is kept well-repaired by patching, it will greatly lengthen the life of the bricks in this part of the furnace.

Boiler furnaces are not usually supplied with a high quality of firebrick except at the bridge. In fact, "boiler" firebricks are often regarded as the lowest quality produced by good firms. This is a mistake. For Lancashire and Cornish boilers, a refractoriness corresponding to Seger Cone 26 is usually more than sufficient; these boilers are less exacting than water-tube boilers, as the arch of the latter is usually played upon by the gases from the furnace and must be able to resist the sudden changes in temperature to which it is subjected each time the furnace door is opened.

The temperature attained in boiler furnaces is not nearly so high as in some other kinds of furnace, so that the refractoriness of the bricks needs less consideration. Attention should, therefore, be concentrated on (i) the insensitiveness of the bricks to sudden changes in temperature, (ii) their resistance to corrosion by flue-dust and imperfectly burned gases, and (iii) the mechanical strength of the bricks. The first two of these requisites demand directly contradictory properties, (i) requiring porous bricks and (ii) those with a close texture. The best results are obtained by using porous bricks with a very dense " skin " or surface, the bricks being renewed when this " skin " has worn away. Hollow blocks with thin walls of close texture appear to be better than solid bricks, where no heavy load is to be supported, especially if a current of cool air can be passed through the blocks.

The *combustion chamber* of a boiler furnace should always be lined throughout with firebricks, so that the flame and hot gases do not come into contact with metal until the combustion is complete; otherwise, they will be cooled and the above-mentioned troubles may occur. This precaution is particularly necessary when oil or gas is used for firing boilers, though its importance in coal-fired boilers is not sufficiently appreciated by many engineers.

A serious defect in many boiler furnaces is a combustion chamber which is so short that the gases from the fuel are cooled by the tubes or plates and so cannot be properly burned. The cooling causes the deposition of carbon in the pores of the bricks, whereby the latter are made to flake or spall. The provision of a sufficiently large combustion space overcomes this difficulty and increases the efficiency of the boiler, whilst simultaneously lessening the amount of smoke produced and increasing the durability of the firebricks.

The durability of a boiler *setting* is greatly influenced by the stoking; mechanically fed boilers are usually more durable owing to the greater uniformity of the combustion. In firing by hand, it is extremely difficult to secure a high degree of uniformity of combustion, and this irregularity has a detrimental effect on the settings.

On account of the rapid variations in temperature, especially in hand-firing, it is preferable to use fireclay or grog bricks for boiler settings. Silica bricks will withstand a high temperature without softening, until the critical point is reached, but they then fail suddenly. They also have the disadvantage of being unable to withstand sudden changes of temperature. Under the pressure of the boiler and overlying brickwork, the crushing strength at a high temperature is reduced; that is to say, a firebrick which will stand under a load of 50 lbs. per square inch when cold, will fail under the same load at a temperature of 1400° C. In constructing boiler settings, care must, therefore, be taken not to overload the bricks which are subjected to the highest temperatures. A load of 25 lbs. per square inch appears to be quite safe at any temperature likely to be reached in connection with a boiler setting. No bricks should be used for the hottest parts of the setting which will not endure a load of 40 lbs. per square inch at 1350° C., or a temperature of 1690° C. without any load.

Bauxite bricks are made of a mixture of bauxite and fireclay and are intended to resist specially high temperatures. It is seldom necessary to use them in boiler settings, as fireclay bricks are equally durable (if carefully selected) and much cheaper. The greater resistance to high temperatures which bauxite possesses is of little or no advantage in most boilers, as the temperatures attained are not sufficiently high for the advantages of the bauxite to be exhibited.

Whether fireclay or silica bricks should be employed will depend on the coal used for heating the boiler to a large extent. If this contains a large amount of pyrites and so evolves sulphur and acid products, silica bricks will probably wear the best, but fireclay bricks will withstand any ordinary proportion of sulphur in the coal. If the coal is high in ash (say over 5 per cent.), it is better to use fireclay bricks which have been made of rather fine material and have a close-textured surface of a partially vitreous nature. Such a surface will withstand the chemical and abrasive action of the dust and ash much better than any ordinary silica bricks can do, and so will wear much longer. For this kind of work, however, the firebricks must be well made and must have been very well burned. The half-baked products sometimes used for boilers because they are cheap are no use where coal is rich in ash or dust-forming material. Some engineers build the sides of the settings with fireclay bricks and the roof with silica bricks; this is a refinement which is seldom really necessary, and is probably based on an experience of low-grade fireclay bricks. There is nothing against it, except the additional cost of using bricks of two kinds and the possibility of the silica bricks spalling.

The use of magnesia bricks has sometimes enabled engineers to overcome lack of durability when burning a coal with an ash which is very rich in lime. If magnesia bricks are used, they must be backed with chromite or other neutral bricks in the hottest part of the setting, or they may combine with fireclay or silica bricks and so collapse, because the combination has a lower melting-point than either of the separate materials. At present they are too costly for boiler settings.

The firebricks used in a boiler setting should preferably be made from fireclay and grog, the particles of grog being ¼ to ⅜ inch diameter, and the raw fireclay being ground so that it all passes through a 30-mesh sieve. The large pieces of grog enable the bricks to stand sudden changes of temperature, whilst the clay keeps them well together and produces a texture which wears very uniformly. They should be burned at Cone 10 to make the bricks sufficiently hard to be durable, and should be as accurate and regular in shape as possible, so that the joints may be quite thin; they ought not to be more than ⅛ inch at the thickest part, and the closer the bricks are together the more likely is the setting to remain tight. The firebricks may be laid in a slip or slurry made of the same material as the bricks, ground with sufficient water to give it the required consistency.

In locomotive fire-boxes, the arch should be constructed of good firebricks, which may be glazed, and so made more durable by throwing a bucket of sand under it when the engine is at work for the first time. Arches made of firebricks of ordinary size have the disadvantage of requiring a large number of joints, which are causes of weakness; such arches have a shorter life than those made of larger blocks. The former have the advantage that small bricks can be introduced into the fire-box through the fire-hole. On the other hand, a smaller number of blocks—say eighteen to twenty in number—can be made of considerable length, whilst their width is so arranged that they can pass through the fire-hole. On some railway locomotives, arches made of three large moulded blocks last so well that they are worth the extra trouble incurred in putting them together.

It has been noticed that a brick arch with a rough or irregular surface is more effective in breaking up the currents of mixed gas and air, with the result that the arch becomes more highly heated. It would, therefore, appear advantageous to build arches with irregular faces on the under side and front edge. In some locomotive arch blocks, the under sides of the blocks are made with pockets which act as baffles, so that the air and gases strike this "rough" surface and are thoroughly mixed, whilst in another form, which has given very good results with inferior coal, the arch is built up of ordinary firebricks arranged with " pigeon-holes " which pass through the arch.

A remarkable development in the use of firebricks for boiler settings has taken place in recent years. Only a few years ago the term " boiler brick " was synonymous with a second- or third-rate material. To-day, no fireclay brick is considered too good by the best engineers if it materially lengthens the service. For the side walls, many engineers find that bricks suitable for blast furnaces are economical, and even expensive bauxite bricks are sometimes used because of their greater resistance to clinkering. Under modern conditions, with large grate areas, mechanical stokers, forced draught and boilers working from 50 to 150 per cent. over the rated capacity, the problem of constructing a durable boiler setting is no small one.

The *bridge* in a boiler requires to be made of better material than the remainder of the furnace, as it is subject to the action of flue-dust, flame, hot gases, and rapidly varying temperatures. In consequence, it should be built of open, coarse-textured bricks, the surface nearest the fire being made of dense material. The refractoriness of the bricks must be high (Seger Cone 31 or 32), as the conditions are very severe and the heat resistance is rapidly lowered by the action of the dust (ash) and gases which corrode those parts of the bricks with which they come in contact.

Some bridges have a hollow interior through which cold air is passed; this necessitates the bricks being insensitive to sudden changes in temperature and, therefore, of coarse texture.

Many defective settings may be avoided if the engineer ordering the bricks would state the particular defects he wishes to avoid, always bearing in mind that he cannot have a brick which will be of the highest quality in every respect, such as one which, with the utmost resistance to high temperatures, also possesses the maximum resistance to abrasion.

It is a good practice to build a parting or partition between the lining and the outer course of the setting with diatomite bricks. The latter have an exceptionally great resistance to the passage of heat through them, though they are too friable to be used in the construction of those parts of the setting which come into direct contact with the flue-gases. By reducing the radiation, such a parting effects considerable reduction in coal consumption and rapidly pays for the extra trouble taken.

It is also well to have the outer facings of the setting composed of vitreous bricks so as to keep rain from penetrating the flues, and flue-gases leaving the boiler other than by the chimney.

The chief precautions in selecting bricks for boilers are to see that they are made of good fireclay, or of fireclay and grog, are well-burned, have a close and regular texture and are accurate in shape and size, so that they can be laid with thin joints. If bricks of low quality have to be used, they should not be employed in the bridge, nor in the arch above the grate and bridge. Where the conditions are exceptionally severe, as in some kinds of water-tube boilers, it is advisable to use high-alumina bricks, which may be of the sillimanite or mullite type.

In **brass-melting furnaces** (crucible furnaces) of the pit type (fig. 168), in which a crucible is used and coke or oil is the fuel, highly refractory and well-burned fireclay bricks of medium coarseness give the best results and will resist the action of fused coke ash and deposits from the oil.

In the tilting type of furnace, the most refractory kind of fireclay brick obtainable is required to ensure good results. The bricks should be dense and hard-burned to resist the action of the oil or gas and air which are usually admitted under pressure. The slags created by brass are very scouring and, consequently, do not permit the use of open- or coarse-grained bricks. Specially shaped bricks are usually required for this type of furnace, to avoid the number of joints which occurs in lining it with standard bricks. Many brass-melting furnaces are lined with wet, ground ganister, carborundum sand, or a mixture of 70 parts carborundum fire-sand, 15 parts ground fireclay, 8 parts water-glass, and 7 parts water, which is very satisfactory and can be repaired readily, but the high thermal conductivity of carborundum is objectionable. Bricks made of fused alumina are particularly suitable, but very costly.

Calcining furnaces are used for heating materials so as to deprive them of water or other volatile material, or to effect other changes, due to heat, which may be desired. The most usual types of furnaces used for calcination are reverberatory furnaces and shaft furnaces. The chemical action of the calcined material on the brickwork must be considered, though the chief destruction is wrought by abrasion, as the temperature of calcination is seldom high enough to affect the brickwork. Hence, almost any good quality of firebrick may be used, preference being given to those with a close, hard surface, so as better to resist the abrasion of the contents.

Cement-kilns.—In the manufacture of cement, *shaft-kilns* were at one time exclusively employed, and they are still used. The bricks suitable for lining them are the same as for lime-kilns (p. 782), but, as the conditions are more severe in cement-kilns, care should be taken to avoid inferior bricks in the hottest zone.

For *rotary cement-kilns*, see p. 791.

Chemical Furnaces.—In the manufacture of chemicals, very few types of furnaces are used, but the variations in them are large on account of the necessity of stirring the contents or subjecting them to other special treatment. These variations sometimes affect the design and operation of the furnaces in an unexpected manner, so that the construction of furnaces for chemical manufacture is largely based on experience and only slightly on scientific principles.

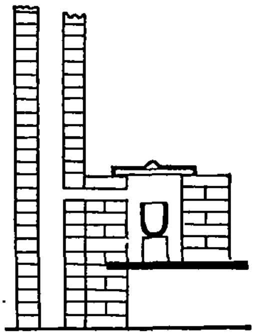

Fig. 168.—Crucible furnace.

Reduction furnaces are usually of the lime-kiln, blast-furnace, or cupola types (*q.v.*).

Oxidation furnaces are usually of the open-hearth, reverberatory, or muffle types (*q.v.*), but for some purposes a simple container of cast-iron or burned clay heated by passing hot gases below and around it is sufficient.

In selecting refractory materials to be used in the construction of chemical furnaces, it is essential to take into consideration (*a*) the maximum temperature to be reached, (*b*) the variations in the temperature in heating and cooling, (*c*) the action of acid and other vapours or gases, (*d*) the action of the chemicals to be treated, (*e*) the action of dust and other adventitious constituents of the flue-gases, and (*f*) the abrasive action of rakes, pokers, and other tools. The desirability of a porous or dense material will depend chiefly on the amount of corrosion likely to occur, it being a general rule that the more porous the refractory material the more likely is it to be corroded. On the other hand, a porous material is less sensitive to sudden changes in temperature. A wise plan is to have a thin and easily renewable lining of dense material for those parts more subject to chemical corrosion and to use a more porous material for the remainder of the furnace.

Due consideration should also be given to the fact that acid chemicals require the use of silica or fireclay bricks, whilst for alkaline and basic chemicals preference should be given to magnesia, dolomite, alumina, or neutral bricks. When alkaline or basic chemicals must be heated in a furnace built of silica or fireclay, the choice of a good lining is very difficult. In the case of lime compounds, for instance, silica is preferable, as the calcium silicates are usually less fusible than the calcium alumino-silicates derived from clay.

Bauxite bricks and bricks of fused alumina are much more resistant, but so expensive that the tendency is to use fireclay bricks and to coat them, where necessary, with a highly aluminous refractory cement.

Even where the charge is basic or alkaline, high-alumina bricks are usually more durable than magnesia bricks—particularly if water or steam is present or the temperature changes frequently.

It is also a matter of great importance that the bricks, blocks, etc., used in the construction of chemical furnaces should be as constant as possible in volume when in use, though this fact is usually overlooked. If the bricks either expand or contract seriously in use, the furnace will not be durable. The only way to prevent serious changes in volume is to use bricks which have been burned at a sufficiently high temperature; cheap firebricks are usually under-burned.

Any unavoidable expansion or shrinkage must be allowed for when building the furnace.

The mechanical strength of bricks and blocks, and especially that of slabs and tiles used in chemical furnaces, is also important, though no general rules have been formulated with regard to it. Mechanical strength is usually secured by the employment of hard-burned material, and, as the latter is requisite to resist chemical action and to avoid shrinkage, mechanical strength does not usually require special attention.

Checker bricks are used in regenerators, etc. (see p. 785).

Coke ovens are used for the conversion of coal into coke and other by-products, and usually consist of a long series of chambers, each forming a retort and heated, as far as possible, by waste heat from previous chambers. The design of these ovens necessitates the use of bricks which will withstand temperatures up to 1400° C., are not affected by sudden changes of temperature, and are perfectly constant in volume. Bricks which shrink or expand to any considerable extent are quite unsuitable for coke ovens.

The most suitable bricks for general use in coke ovens are grog bricks or silica bricks[1] of high refractoriness and moderate porosity; they must have been burned at Seger Cone 14 or above in order that they may resist heavy loads and that their volume may be constant when in use.

It is preferable to use different kinds of bricks in various parts of the oven, silica bricks or very porous grog bricks being excellent in the crown; denser grog bricks are better for the lining, and vitrified clay bricks are best for the bottom of each cell or chamber on account of their resistance to abrasion, especially as this part rarely reaches a temperature above cherry-red heat.

The most important feature of coke-oven bricks is that they must have great constancy of volume: this is essential.

The curves in fig. 169, due to Baron Coppée, show both the expansion of

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[1] Silica bricks of such a composition that they neither expand nor shrink in use are rapidly superseding clay bricks for coke-oven work. This is due to the difficulty of purchasing satisfactory clay bricks; the latter, if properly made, are better than those of silica. For coke ovens, a brick which has met with great favour in the North of England is the one locally known as a "half-ganister" brick—that is, a brick made by mixing fireclay and ganister. It is difficult to avoid excessive shrinkage in *bauxite* bricks.

various bricks with increasing temperature and also the temperatures at which different bricks begin to fuse. The temperatures are plotted as abscisssæ and the expansions (in thousandths) as ordinates. The curve A refers to a Belgian brick, and it will be seen that it expands regularly up to about 650° C., at which temperature it reaches a maximum dilatation of a little over $\frac{5}{1000}$, or about 0·5 per cent., and when heated further no more expansion takes place. Similar curves have been obtained with another Belgian brick, B, and a German brick, D. C is a French brick. These four are good bricks eminently suitable for coke-oven construction. H is a brick of English origin, which has a rather high expansion, but is otherwise good. The bricks E and F, which are of French manufacture, reach a maximum expansion at about 800° C. and 900° C. respectively, after which they commence to contract. Another English brick, K, has the same characteristics, though to a less extent. It is evident that bricks which behave in this manner are unsuitable for coke-oven construction, inasmuch as the contraction would set up cracks and dislocations in the oven structure, thus allowing direct communication between the coking chamber and the heating flues, with consequent loss of gas and by-products. Another English brick begins at about 900° C. to develop cracks and fissures, which render it useless, though it has a refractoriness of Cone 29.

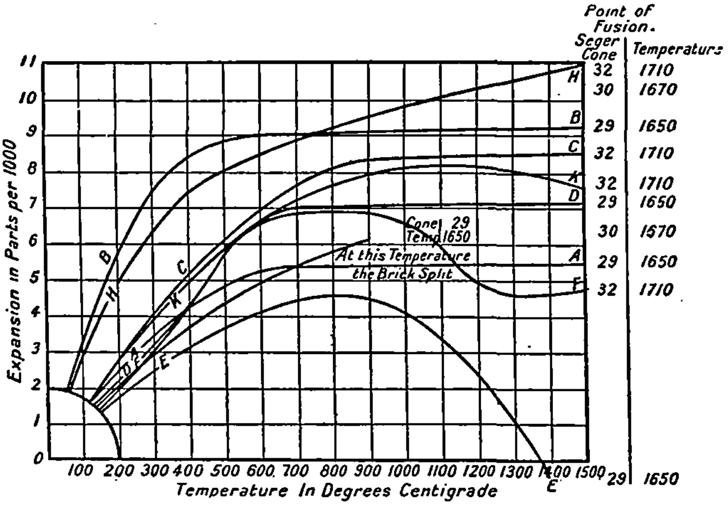

FIG. 169.—Expansion of firebricks.

This illustration must not be understood to mean that British firebricks are not as suitable as Belgian bricks for coke ovens, for precisely the contrary is the case, and brick manufacturers in this country can supply perfectly satisfactory bricks for this purpose if provided with the requisite specifications. Without such specifications, it is quite possible that under-burned bricks which either expand or contract when in use will be supplied.

There is much controversy as to the relative advantages and disadvantages of fireclay and silica materials for lining coke ovens. Fireclay bricks—unless exceptionally well-burned—have the disadvantages of contracting in use and are, therefore, liable to crack. Silica bricks, on the contrary, expand in use, though any damage may be avoided by heating them very carefully, after which there is little danger of abnormal injury to the ovens. Silica bricks have the advantage of not softening until very close to their fusing-point, so that they are less likely to fail in the oven than fireclay bricks, which, on prolonged heating, tend to sag. If silica bricks have a greater heat conductivity than fireclay bricks, the heat will be conducted more rapidly, and the temperature in the oven will be higher or the speed of coking greater than when fireclay bricks are employed. Silica bricks in coke ovens have a considerably longer life than fireclay ones, and they are also less likely to be seriously damaged by careless heating, which may cause slagging or fusion in the case of fireclay bricks, but they are more liable to spall. The quantity and quality of the gas-coke and by-products are also decidedly in favour of silica bricks. The chief disadvantages to the use of silica bricks for coke ovens are (*a*) the danger of spalling and abrasion; (*b*) the smaller amount of ammonium sulphate produced as a result of the higher temperatures attainable and, therefore, used. The following table by J. Enzenauer[1] shows a comparison between coke ovens lined with silica and fireclay materials respectively:—

TABLE CVI.—COMPARISON OF SILICA AND FIRECLAY BRICKS IN COKE OVENS.

	Silica Bricks.	Fireclay Bricks.
Ovens emptied per 24 hours	65	54
Time of working a charge (hours)	24	29
Weight of coal (dry) per charge (tons)	7	7
Weight of coal (wet) per charge (tons)	7·8	7·8
Weight of coal (dry) treated per hour (tons)	18·96	15·91
Gas consumption per hour (cub. ft.)	126,370	105,600
Heat consumption per ton of dry coal (cals.)	692	697
Temperature in horizontal passages (deg. C.)	1,069	1,027
Temperature in exhaust flues (deg. C.)	372	327
Temperature in coking chamber, final stage (deg. C.)	908	804
Temperature of crude gas in upcast (deg. C.)	456	434
Temperature of crude gas in receiver (deg. C.)	295	270
Temperature of crude gas in suction main (deg. C.)	275	249

He found that the silica bricks are more resistant to salty coal, slagging, fusion, and mechanical abrasion than fireclay bricks, and, contrary to expectation, the yield of sulphate was not impaired, the coke was of better appearance, and considerably harder than from ovens built of fireclay. On the other hand, fireclay bricks are more satisfactory for some purposes. Thus, washed coals are preferably coked in ovens lined with fireclay bricks, as those containing a moderately high proportion of alumina are more satisfactory than those composed wholly of silica in the presence of much moisture.

A. H. Middleton,[2] after an extensive examination of coke ovens in the United States, has concluded that silica bricks containing about 97 per cent. of silica are the best for coke-oven linings, on the grounds that, as compared with fireclay bricks, they (*a*) give an increased output of coke, (*b*) have a greater thermal efficiency, (*c*) have a greater durability, (*d*) offer a greater resistance to corrosion by salty coals, and (*e*) offer a greater possibility of varying the heat-treatment where different classes of coal are to be coked. He does not appear to share the fears of others that silica bricks are too sensitive

[1] *Iron and Coal Trades Rev.*, 1921, p. 102.

[2] *Gas World, Coke Sect.*, 1922, pp. 17 and 23.

to sudden changes in temperature. His conclusions are supported by tests at the Duisburg Steel Works, which showed that coke made in silica retorts has a better appearance than that from clay retorts, that the coking was complete in twenty-four hours as against twenty-nine hours in clay retorts, and that, with care, the silica retorts could be extinguished and relighted without damage.

Silica bricks are almost exclusively used in American coke-oven practice, and they are being increasingly used in this country, especially for salty coal, though their quality—particularly as regards the properties conferred by prolonged heating at 1500° C.—needs to be improved considerably before they can be pronounced perfectly satisfactory.

In the British Isles and in Germany, silica bricks are used in all the new coke ovens because, in spite of the disadvantages mentioned, they are, on the whole, more satisfactory. They must be made to conform to close specifications, the purpose of which is to ensure that the bricks shall be constant in volume when heated and that they shall resist the action of salt, steam, and other corrosive agents. Great accuracy in shape and size is essential.

In many coke ovens, a compromise has been made between silica and fireclay bricks by using a mixture of crushed silica rock or ganister and fireclay, the proportion of silica being 80 to 85 per cent. (see " half-ganister " bricks, p. 462). Such mixtures undergo practically no change in volume on heating, as the contraction of the clay is counterbalanced by the expansion of the silica. Some naturally siliceous clays have also been used for the same purpose.

The inside of coke ovens may be constructed of hard-fired silica blocks of the required shape, except near the door, where the temperature variations are rather great and fireclay bricks or blocks are more durable.

The roofs of coke ovens may be lined with about 9 inches of hard-fired silica bricks, backed by several courses of fireclay bricks, the latter being protected by red bricks, and, if desired, a course of insulating bricks may be included. The whole may be capped by vitrified paving bricks as a protection against the weather.

Where several coke ovens are built together and only separated by division walls, the latter may well be constructed of well-fired silica bricks of uniform size, great strength, and high heat conductivity.

As a general rule, silica bricks for coke ovens should not have more than 1·65 per cent. of alumina, and they should be made from materials crushed to such an extent that 97 per cent. will pass through a ¼-inch mesh screen.

The silica bricks used for the foundation walls and linings should have a crushing strength of not less than 1600 lbs. per square inch, whilst for less important parts a strength of 800 lbs. per square inch is generally sufficient.

Fireclay bricks used in coke ovens should not show more than 1 per cent. expansion, or 1·6 per cent. contraction, when reheated, and their size must not vary more than ⅛ inch per foot for bricks or blocks which are less than 12 inches long, nor more than $\frac{3}{16}$ inch for larger blocks.

Magnesia bricks have not been very successful in coke ovens on account of the cost and the difficulty of spalling. Recently, magnesia blocks enclosed in a thin iron casing seem to have been somewhat more successful.

Chromite bricks, owing to their extremely neutral character, have been tried, but there is not sufficient data as yet to determine their value.

Zircon bricks suffer from the disadvantage of high cost, but their extremely inert character may prove sufficiently advantageous to warrant more extensive trials.

Two classes of carborundum materials have been used in coke ovens—solid bricks and veneered bricks. The solid bricks are much stronger mechanically, and their extra cost will probably be compensated for by a longer life, but they cost about thirty times as much as fireclay materials.

With all these inert materials, the adhesion of slags to the sides is eliminated, along with any corrosive action which might take place, and this also results in a decrease in the time required for cleaning the sets, as the barring down with high fusing ashes is eliminated.

The parts of the coke oven which it is most difficult to keep in good condition are the four lower courses, the upper parts, from the charging hole downwards, being also attacked to a greater or less degree, particularly when wet coals are distilled.

The principal causes of deterioration and decay in coke ovens are—

1. Unskilled management.
2. Wet coal.
3. The presence of salts in the coal.

When coke ovens are charged with coal rich in salts, it is important that the bricks should present a close surface to the coal, as coarse, open bricks are more readily attacked. The bricks must have a porous body behind the close surface, or they will not withstand sudden changes in temperature.

Salt or ash in the coal is regarded as a cause of many defects in the bricks, but the evidence is by no means clear. The salt commences to decompose and volatilise at about 800° C., but as the temperature in the interior of a coke oven is not usually sufficient to produce a glazed surface on the bricks, the vapour of the volatilised salt does not react with the surface of the bricks in the ordinary way, but penetrates them and to some extent is deposited in the pores. The remainder passes through the brick until it reaches the hotter exterior, where the interaction between the clay and salt takes place with greater rapidity. The varied rate of interaction tends to form a very porous and friable mass, which is fairly rapidly disintegrated if the action of the salt becomes serious.

There is also a tendency to form layers of iron oxide, because the interaction of the salt and the iron compounds in the clay form ferric chloride, which is decomposed and deposited in layers on reaching the oxidising zone. The formation of oxides, etc., in the bricks causes disintegration on account of their different coefficient of expansion on heating.

Fireclay bricks seem to be attacked much more strongly than either alumina or silica bricks. Alumina bricks cannot usually be employed, as they contract far too much in use, but silica bricks may be very satisfactorily employed for coals which contain a considerable proportion of salt. Glazed fireclay bricks have been tried for coke-oven linings, but they have not been successful on account of the difference in the coefficient of expansion of the body and glaze, as a result of which the glaze soon scales off and exposes the fireclay to the action of the salt.

According to A. H. Middleton, the trouble caused by the action of salt can be entirely avoided by using bricks made of almost pure silica instead of ganister or a silica rock containing 77 to 85 per cent. of silica. The suggested immunity of bricks made of almost pure silica is remarkable, but it is based on observations of ovens built with almost pure silica and those built of ganister bricks. No explanation is offered for this difference in behaviour; it appears to be due to the action of the salt on the clayey matter present in the mixtures containing less than 85 per cent. of silica. Ammonium chloride is the principal corrosive agent in salty coals, and it is assisted by common salt (sodium chloride) and ferric chloride. Bricks which have been used in coke ovens sometimes contain ammonium alumino-silicates formed by the action of ammonium chloride in the coal on the clay in the bricks. An excessive sintering of the surface may account for the shortened life of some bricks in coke ovens, though some other reactions probably also occur, as the molten layers often contain a higher percentage of alumina (and less silica) than the average composition of the brick.

The interaction of the carbon and any salts in the coal with the clay at high temperatures must also be taken into consideration in endeavouring to learn the causes of defects in the refractory material.

Another cause of disintegration in coke ovens is the deposition of carbon in the pores of the brick. This carbon is due to the decomposition of hydrocarbons in the coke-oven gas or in the gases in the outer flues in the presence of clay. Such carbon occasionally effects the rupture of the pores of the brick and may cause it to break up completely. In some ways, the action appears to be catalytic and to be due to the fireclay itself, as the same substances, when heated under precisely similar conditions in the absence of fireclay, require a higher temperature for the formation of free carbon. Unfortunately, the experiments hitherto made are by no means conclusive on this point.

The iron oxide in the bricks may also be reduced to the ferrous state by reducing gases in the interior of the oven, and may form a fusible compound.

Flue-dust—which is chiefly derived from the coal burned in the oven—is commonly rich in lime and other bases, and also acts like salts. Arrangements should be made to keep it in as cool a part of the flue as possible, so that it may not be hot enough to exert a slagging action on the brickwork. If the face of a coke-oven brick which has been in use for some time be chipped off and both it and a portion of the interior of the brick are analysed, it will be found that the face is richer in lime and alkali than the interior. Sometimes a curious increase in the proportion of silica also occurs in the face of the bricks, suggesting that some kind of volatilisation of silica occurs, particularly near the top of the oven.

Sulphur in the coal may be oxidised in the presence of steam, forming sulphuric acid, which attacks the bricks, though this action is seldom as extensive as some coke oven managers suppose.

Wet fuel is far more serious than sulphur, as superheated steam has a strong softening effect on both fireclay and silica bricks, especially when they are porous. When large coal is carbonised, the effect of moisture in it is not very serious, but the effect of washed coal on the coke-oven bricks is highly detrimental.

As regards both the stability and durability of a coke oven, the customary practice of dropping wet coal into a red-hot chamber is most unsatisfactory, and is one reason why vertical shaft ovens should be more durable than those of the multiple-chamber type. The salts in the water used for washing the fuel often have a deleterious action on the oven, as they are decomposed by the brickwork in the manner already explained for salts generally.

The effect of prolonged or repeated heating on coke-oven bricks is to cause them to soften and collapse. Before softening takes place there is also the difficulty of the expansion or shrinkage of the bricks. In multiple-chamber ovens any appreciable amount of movement in the brickwork may endanger the stability of the structure, and it is almost certain to cause trouble with deformed flues. The only preventative of such movement is to take precautions that only fully burned bricks are used. The author is accustomed to insert, in specifications he draws up for those of his clients who buy bricks for coke ovens, a clause to the effect that the bricks must be burned at a temperature not less than 100° C. above the highest likely to be attained in that part of the oven in which the bricks are to be used.

The longer the bricks are heated, the greater will be the change in their dimensions, but if they have been sufficiently well burned in the course of manufacture, any subsequent changes in use will be unimportant. Where, however, bricks which have been burned at 1300° C. or less are used for the hotter parts of a battery of coke ovens, trouble due to expansion or shrinkage is almost certain to occur.

The best bricks for coke ovens, if accurately measured whilst being heated, will be found to expand slightly up to about 600° C., after which no further change in volume will take place. Bricks which either expand or contract at higher temperatures are not suitable.

These considerations all show how unreasonable it is for coke manufacturers to expect a guarantee as to the durability of the coke ovens, though they undoubtedly have a right to the most durable materials available.

There is a tendency on the part of engineers and oven builders to attribute all defects to insufficient refractoriness of the bricks. This is a mistake, as some bricks which are apparently admirable in many ovens are useless in similar ovens in other districts, a state of affairs which is difficult to explain, except on the assumption that it is the coal or the management of the ovens which is at fault. The only way in which such difficulties can be overcome is for the coke manufacturers to unite with the makers of bricks and blocks used in coke-oven construction, with a view to the defects being studied more systematically and thoroughly than is possible for either party to do without the other.

The principal requirements, therefore, of coke-oven bricks are:

1. They should resist a temperature of 1400° C. for an indefinitely long time.
2. They should be sufficiently strong to resist the pressure of the brickwork.
3. They should be fairly gas-tight, and the cement used to bind the bricks must also be gas-tight at the temperature attained in use.
4. The bricks must be sufficiently resistant to abrasion to resist the abrasion caused by inserting and withdrawing the materials from the oven.
5. They must be resistant to any impurities likely to occur in the coal at the highest temperatures attained in the coking process.

All bricks used in the construction of coke ovens should have a good " ring "; if they have not this quality they should be rejected. In some cases, dampness may cause them to emit a dull sound when struck, in which case allowance must be made. A dull " ring " is generally due to the presence of small cracks, which may be serious, so that it is necessary to take great care in the selection of coke-oven bricks.

It is undesirable to cut bricks which are to be used in coke ovens, as it reduces their strength. The presence of iron stains in the bricks is not usually important, unless it is found that, in actual use, the bricks are seriously corroded around the iron stains, in which case the bricks should be rejected.

Converters are furnaces used to transform iron into steel by oxidising the carbon and silicon contained in the former, or to transform copper matte into metal by oxidising the sulphur and iron. No added fuel is used, but an intense heat is generated by means of an air-blast which effects the oxidation.

Such converters are usually lined with silica bricks of special shape to fit the rotundity of the furnace, or with ganister, the latter being made into a wet paste and rammed into position with the aid of wooden forms. In some converters, the lining of silica bricks is coated with ganister paste (see "Copper-working furnaces," *below*).

Basic linings for converters are made of magnesia bricks or dolomite. These bricks or blocks may be 15 inches thick at the sides and 2 feet at the bottom. They are laid in anhydrous tar. The bottom is sometimes laid separately, burned in a kiln to drive off the tar, and then placed in the converter. By hinging the iron bottom to the converter and using a loose basic bottom, repairs are facilitated. (For further information on basic linings, see "Steel furnaces," p. 794.)

Copper-working furnaces are used for a variety of purposes, the chief of which are roasting, smelting, and "converting." An important part of copper-smelting furnaces is the "settler," in which the slag and metal are separated. The settler should be lined with magnesia or chromite bricks, though fireclay bricks are often used, the matte tap-hole being lined with chromite or carbon bricks.

Copper converters are large vessels mounted on trunnions and lined with refractory materials. They are heated by a powerful current of air which oxidises the sulphur and iron. The linings may be *acid, i.e.* made of silica or fireclay bricks, or of quartz or ganister bonded with fireclay, rammed into position by hydraulic pressure, or *basic, i.e.* lined with magnesia bricks.

Copper-roasting furnaces are similar to the roasting furnaces described on p. 791. The multiple hearths are usually made of fireclay bricks, the walls being built either of good red or fireclay bricks. Occasionally, the interior of this type of furnace is built wholly of magnesia bricks.

Copper-smelting furnaces were formerly of the blast-furnace type, but these are rapidly being displaced by reverberatory furnaces, which, when suitably designed, produce an equal output at much less expense. In reverberatory furnaces used for smelting copper, the bottom is usually composed of sand or crushed quartzite, which, when in position, is fused superficially so as to form a resistant hearth. In Swansea, sand from the seashore is used for this purpose, as the bases in it are sufficient to cause the necessary partial fusion of the sand. Where quartzite is employed, as in America, it is necessary to add a fluxing agent, such as felspar. Unfortunately, sand-hearths are very wasteful, as they absorb so much copper—100 tons of this metal having been found in such a hearth. It is, therefore, more economical to construct the hearth of dense firebricks laid in a mixture of ground fireclay and foundry coke. Of the various bricks which have been used for such hearths, silica bricks are excellent if properly made, but otherwise they are unsuitable, as they expand too much and so destroy the hearth; fireclay bricks—if properly made and of good quality fireclay—are usually quite satisfactory; magnesia bricks have been used in reverberatory furnaces for the treatment of foul blister copper, and are much less corroded and cause the formation of less slag than silica bricks, but unless very well burned they spall. Chromite bricks are more satisfactory than magnesia bricks for copper-smelting as regards the amount of corrosion, cracking, and spalling, but they absorb too much metal. One firm overcomes this drawback by grinding up the old bricks, treating the powder to recover the copper, and using the residue for making new bricks. On the whole, dense fireclay bricks, containing about 30 per cent. of alumina and rich in grog, form the most suitable material for the hearths of copper-smelting furnaces. The sides may also be built of fireclay or silica bricks.

Copper alloys are usually melted in fireclay crucibles, or in reverberatory furnaces or rotary furnaces provided with a lining of fireclay bricks. These need not be of great refractoriness, but they should be accurate in shape and well burned.

Core stoves are used for drying and heating cores in foundries. The temperature is never very high, so that they may be constructed of red bricks, with the exception of the fireplace and combustion chamber, which should be of second quality fireclay bricks.

Crucible furnaces are of several types and manifold uses. Those employed for the more fusible materials may be regarded as brass-melting furnaces; those required for high temperatures are preferably constructed like those used for making crucible steel.

In this country, crucible-steel furnaces are simply rectangular pits lined with ganister, so as to leave a circular opening somewhat larger than the crucible. Coke is burned on a grate at the bottom of the furnace, the crucible being surrounded by the fuel, which, in turn, is enclosed in the furnace. This is built of firebricks and lined with a monolithic lining of ganister formed by placing a wooden block in the centre and filling the space between it and the brickwork with tightly rammed ganister paste. The block is then withdrawn, and the lining is dried and then heated until it is hard. More recently, refractory cements have been used instead of ganister, but all these monolithic linings are less durable than those made wholly of good bricks of the correct shape. Bauxite and other high-alumina bricks have been used and are satisfactory, but are regarded as too expensive. The firebricks used for such linings must be of good quality and shape, and, on laying them, the builder should " rub " them on all the jointing sides so as to ensure as thin a joint as possible. Before laying, it is well to damp them a little so as to prevent them absorbing moisture from the " cement " or mortar.

A great improvement may be effected by building the furnaces of silica bricks or of open, coarse-grained grog-clay bricks, and heating them with gas instead of fuel. The gas used is producer gas, both it and the air-supply being heated regeneratively. By this means, the life of the furnace may be increased to about three times the present average life of ganister-lined furnaces. When the coke used is rich in salt or ash, magnesia bricks are preferable to those of silica or fireclay, but require great care in use on account of their sensitiveness to sudden changes in temperature. Linings of fireclay bricks have not proved durable; grog and bauxite bricks have not been used sufficiently for their value to be known. For most crucible furnaces, fireclay, grog, or silica bricks are the best; some users insist that the mouth or pot-hole should be built exclusively of silica bricks.

Crucible furnaces are subject to sudden and great variations in temperature and should be made of hard-burned, porous, coarse-grained bricks, particularly in the upper parts; the lower parts, which are protected from the air by the fuel, may be of close grain, so as to resist the corrosive action of the ash. Ganister bricks are usually satisfactory and cheaper than grog bricks, which otherwise should be employed.

Cupelling furnaces are of the reverberatory type or the muffle type, the hearth being made of bone ash, marl, cast-iron, magnesia, or chromite. The first three require the hearth to be renewed and re-smelted to remove the lead and silver absorbed. Magnesia is the most satisfactory material for this kind of furnace.

Cupola furnaces are used for melting iron preparatory to casting it in a foundry. They consist of a cylindrical structure with two or more tuyères or air-blasts near the base. The cupola is fed with a mixture of iron and coke, the latter being burned by the air-blast and so melting the metal.

The linings of cupola furnaces must be smooth, dense, fine-grained, hard, and tough, so as to resist the abrasion of the materials and the corrosive action of the slag; they must also be sufficiently refractory (Seger Cone 31 or above to withstand the temperature attained by the contents. It is also desirable that the lining should not be sensitive to sudden changes in temperature To fulfil all these requirements is a difficult matter, and the bricks and blocks which have proved most satisfactory are those made of clay and grog (Chapt. II.), though magnesia bricks may be used satisfactorily when the cupola is under careful management. The tendency to cracking in fireclay bricks may be reduced, in some cases, by the addition of 0·5 per cent. of common salt to the clay.

Silica bricks have been used in some instances with success, but where an effort is made to keep the slag as neutral as possible, grog bricks answer the purpose more satisfactorily than any other kind. It is particularly desirable to use first-class firebricks for cupolas, as the slightly greater cost is more than compensated by the saving effected in repairs and stoppages.

Where cupolas are lined with ordinary firebricks, instead of the regular sections made for the purpose, the bricks should be set on end and one or two lines of ordinary rectangular bricks should be used with the arch bricks. This makes repairing fairly easy, as by forcing out the rectangular bricks the arch bricks can be taken out and new rings can be put in where necessary. By thus renewing the bricks in the melting zone from time to time the necessity of replacing the whole lining does not often arise, and this tends towards economical working. Blocks roughly made of plastic paste and afterwards pressed are preferable to ordinary firebricks. Bricks or blocks made of bauxite or other high-alumina material are satisfactory, but very expensive, and sillimanite bricks appear to be too susceptible to iron-bearing slags to be satisfactory.

For the hottest zones (part of which may attain a temperature of 1700° C.), bricks or blocks made of fireclay and grog, containing more than 35 per cent. of alumina, should be used, and they must be so well burned that they do not shrink appreciably when in use. For the remainder of the lining, good fireclay bricks should be used; they also should be well burned.

The bricks in cupola furnaces wear away rapidly as the result of abrasion and corrosion by slag, so that specially shaped bricks or blocks are advisable, and they must be very accurate in shape and laid with the thinnest possible joints.

The use of monolithic or tamped linings (p. 800) for cupolas is highly approved by some firms and is regarded as unsatisfactory by others. Probably the best procedure is to confine the use of a monolithic material to repairing the brickwork lining. For this a good refractory cement (p. 746) is advisable, and the use of a cement gun (p. 745) for applying it can be recommended.

Instead of a refractory cement, a siliceous clay, composed of small grains of silica naturally coated with a plastic refractory clay, may be used. A mixture of ganister and fireclay, ground with water to form a paste, is also popular, but care should be taken that the proportion of alumina present does not lie between 7 and 11 per cent., or the refractoriness will be too low (see fig. 29).

The grading is important; usually one-third should consist of particles between 5- and 80-mesh, one-third between 80- and 100-mesh and one-third less than 100-mesh, but no grading will suit all cupolas.

Care in heating a cold furnace is essential, if spalling is to be avoided.

With fireclay bricks, the critical temperature is between cold and 800° C., t with silica bricks it is between cold and 300° C.

The damage done to cupolas is chiefly caused by careless or unskilled te struction, drying too rapidly before use, and by recklessly handling the wi rge when using the cupola. A skilful attendant, especially if he is able of daub the lining properly with ganister from time to time, will make a cupola st a far longer time than a less able man; hence the folly of putting an insufficiently skilled man in charge of a cupola, as is so often done.

Cupolas which are chiefly worked with small charges cannot be expected to wear well, as they are subjected to too much abrasion by the materials fed into them. By keeping the cupola full to the charging door, the materials will fall naturally and do scarcely any damage.

Many furnaces must be held with plates and tie-rods to prevent the brickwork from splitting, and, where these rods pass through the brickwork, old gas barrels should be built in for them to pass through. This permits the expansion and contraction of the rods without putting any drag on the brickwork, and allows the easy renewal of broken rods. Where the rods actually pass through a highly heated space, firebrick sleeves should be used to cover them.

Domestic fireplaces may usually be built of material of extremely low refractoriness. It should have a coarse, porous texture with a dense " skin " or surface so as to resist abrasion and yet not be sensitive to sudden changes in temperature. Some manufacturers make firebacks, cheeks, and other parts of domestic fireplaces of fireclay without any addition of grog. This is a mistake, because it produces too dense a material, and is one of the most frequent causes of cracking and splitting. The addition of 25 per cent. of grog (made of old firebricks crushed so as to pass completely through a No. 10 or No. 12 riddle) will avoid these defects in almost every case and need not add appreciably to the cost of manufacture.

Drying stoves are used in foundries for drying moulds and sand-cores. The temperature attained is never high, but it is an advantage to use (second-grade) firebricks as a precaution. Between the interior and exterior of the furnace there should be a layer of insulating bricks (p. 395).

In **electric furnaces,** the conditions are very severe; some parts of an electric furnace are so much hotter than any portion of other furnaces, and the amount of volatilisation which occurs and is accompanied by the deposition of the volatilised matter is so great, that the roof or cover of the furnace is particularly difficult to retain in good condition. An exceptionally powerful reducing atmosphere is usually present, and, owing to the very high temperature attained, the slag is unusually fluid and corrosive. It is, therefore, only natural that no bricks at present on the market are able to withstand all these conditions.

The conditions vary greatly with the purpose for which the electric furnace is used. For example, they are far less severe in smelting iron than in melting steel, and in the manufacture of calcium carbide and some other products no high-grade refractory materials are needed, as the unaltered charge acts as a protection from the heat.

Bearing this limitation in mind, the most important properties which refractory materials for use in electric furnaces should possess are—

1. The refractoriness should be not less than that of Seger Cone 32 (1700° C.).

2. The bricks or blocks should be resistant to sudden changes of temperature.

3. They should be constant in volume at the highest temperatures to which they are exposed when in use, *i.e.* they must have been properly burned at a sufficiently high temperature.

4. They should be resistant to corrosion by both oxidising and reducing gases, deposits, and slags at the highest temperatures to which they are exposed when in use.

5. They should be resistant to abrasion.

6. Except when required to act as electrodes, they should be poor conductors of electricity, so as to avoid undue leakage of current.

7. They should be sufficiently strong when at a high temperature to support the roof and other parts of the furnace above them.

The difficulty occurring on account of the stringent conditions may, to some extent, be obviated by using different materials in various parts of the furnace according to the conditions which obtain. Thus, the outer walls may be made from a suitable heat-insulating material of a moderately refractory nature; the hearth should be highly refractory, inert to slags, and resistant to corrosion by them and by the products of the reactions which occur in the furnace; the roof should be resistant both to slags, fumes, and gases; it should not spall at high temperatures when subjected to sudden changes of temperature, and it must be sufficiently refractory to retain its shape during a long period of heating.

Of the various materials used in electric furnaces, the following are the most important:—

Silica bricks have been largely used where their chemical composition is not deleterious, as they have the advantage of not shrinking and so falling out at the highest temperatures. They are sometimes used in basic furnaces as a lining from the top of the hearth bank to the roof. In such cases, they must be separated from the basic material by one or two courses of chromite bricks. Their chief drawback is their fusion-point, which is not usually sufficiently high to meet the conditions imposed by the hottest parts of the furnace; they also tend to spall when the furnace is emptied.

According to Stobie,[1] some ganisters appear to absorb iron readily, even though their composition and texture are identical with ganisters which do not. This absorption is much more serious in electrical furnaces than in others, but it should not be overlooked in any steel-melting furnace.

Grog bricks of best quality are usually more suitable than silica bricks, but it is difficult to obtain grog bricks of the correct porosity and coarseness. Bricks made of grog or fireclay also soften too readily, and either lose their shape or melt unless the walls are so thin that the heat is rapidly conducted away; in that case, so much heat is lost that the furnace is not economical. Fireclay or grog bricks may, however, be used for the exterior of the furnace. Where a furnace is required to melt basic materials, silica or fireclay linings are useless.

If *fireclay bricks* are used in the roofs of electric furnaces they should have been fully burned, as bricks which shrink in use may have serious consequences. Semi-silica or silica bricks are often preferred as they do not shrink. The best fireclay bricks are generally satisfactory below 1600° C., but they are eventually destroyed by any slag which comes in contact with them.

Bauxite bricks and other *alumina bricks* are being increasingly used, but they are expensive. They may be employed up to 1800° C., and are more resistant to slags than are fireclay or silica bricks.

Chromite bricks are highly refractory and resistant to slags, but are generally

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[1] *Iron Steel Ind.*, 1934, p. 1278.

weak and very expensive. Their chief use in electric furnaces is in those in which a second (reducing) slag is used after eliminating the oxidising slag. The second slag often enters cracks in the lining and causes serious expansion below 700° C., as a result of the formation of dicalcium silicate.

Magnesia bricks are frequently used where the contents of the furnace are basic in character, and especially for the roof, which is usually subject to attack by metallic oxides which are deposited upon it. A material which has proved suitable for lining basic bottoms of electric furnaces consists of 1 part of blast-furnace slag and 10 parts of magnesia, blast-furnace slag being preferred to the basic open-hearth slag which is sometimes employed, as the former is much lower in iron oxide and has a high content of alumina and silica. The hearths of electric furnaces have also been made with a mixture of 20 per cent. of magnesia and 80 per cent. of dolomite bonded with tar.

Where obtainable, bricks made of nearly pure magnesia are preferable, but it was discovered by Rees and Chester[1] in 1931 that unburned bricks are superior for the body of the furnace as they do not spall.

Magnesia bricks, if made of sufficiently pure and fully shrunk magnesia, are of great value in the roof of electric furnaces, and bricks of such material are among the most satisfactory for lining electric furnaces used for making steel by the basic process. If the roof is made of silica bricks and the lining of magnesia bricks, there should be a neutral course of chromite bricks between the other two kinds.

Bricks made of pure magnesia can be used up to 1850° C., but they are mechanically weak and liable to crumble and spall. They are more resistant to basic slags than are any other bricks.

Dolomite bricks resemble magnesia bricks, but the lime in them tends to make them unsuitable when the furnace is not in use.

Spinel bricks (*especially magnesia-chrome bricks*) appear to be particularly suitable for melting steel in electric furnaces.

Sillimanite bricks and mullite bricks behave uncertainly with some slags, but in some electric furnaces they have been found to be very durable, and their use is rapidly increasing.

Zirconia or zircon bricks have not been used to any great extent, though they appear to have a distinct value in electric furnaces. The refractoriness of zirconia and zircon is such as to fit them for use in the hearths, roofs, or side walls, and especially at the slag line. They are very resistant to many electric furnace slags at temperatures well above their fusion-point, and roofs of this material would, in all probability, be found superior in respect to spalling. The heat-insulating properties are also quite suitable.

Silicon carbide (*carborundum*) *bricks* are refractory, but they conduct both electricity and heat and are not suitable for some furnaces. They also tend to introduce carbon into molten metals. They are very suitable for electrically heated muffles.

Kieselguhr bricks are useless as linings, but they are valuable as insulating bricks (p. 395), to be placed between the lining and the casing of the furnace.

The bricks for electric furnaces should be chosen with regard to the chemical nature of the material to be melted in the furnace; for acid or neutral materials, silica or grog bricks are preferable, but for basic materials magnesia bricks are usually essential. It is often best to employ porous bricks of rather coarse texture, but a thin lining of dense tiles, burned at a temperature corresponding to Seger Cone 18 or above, is advantageous in resisting corrosion.

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[1] *Trans. Cer. Soc.*, 1932, **31**, 243.

Unburned bricks (p. 487) made of magnesite, dolomite, or spinel have been used very successfully.

Tamped linings and linings made of refractory cement are largely used in electric induction furnaces where conditions are favourable, but unless very skilfully made are very liable to crack. One of the best methods is to use a metal template having a shape corresponding to the lining to be formed. A dry granular material, such as silica, alumina, or magnesia (with or without flux) which sinters at the desired temperature is placed around the template, and heat is generated until the refractory material sinters. In metal-melting furnaces, the template may be made of the same kind of metal as that for which the furnace is to be used, and it then melts when its fusion-point is reached and forms part of the first charge (Eng. Pat. 226,801—1923).

The chief objection to tamped linings in electric induction furnaces is the tendency to crack if the thickness of the sintered material is insufficient. For this reason, unburned bricks appear to be preferable to tamped linings.

Uses.—Electric furnaces are used for many purposes and the bricks or other materials should be chosen to suit the purpose for which a particular furnace is to be employed.

For general heating in the absence of slags or fluxes, fireclay bricks are generally the best, but silica bricks are commonly used for the roof. For melting metals and alloys, particularly in induction furnaces, the containers were formerly fireclay or graphite crucibles, but they were soon rendered useless by corrosion.[1] It is now customary to use a tamped lining of granular material—usually silica, magnesia, or magnesia-chrome mixtures (spinel); grading is important, and Rees[2] has suggested a mixture of four grades: (*a*) between 5- and 20-mesh 45 per cent., (*b*) between 20- and 60-mesh 10 per cent., (*c*) between 60- and 120-mesh 20 per cent., and (*d*) through 120-mesh 25 per cent.

For melting red brass, rammed linings made of (*a*) fused alumina and fireclay, (*b*) calcined bauxite with a silica bond, and (*c*) magnesia spinel are used.

For melting nickel, nickel-chromium and other alloys and nickel-silver, fireclay bricks are quite suitable, though silica bricks are often preferred for the roof, because their slight expansion lessens the risk of collapse. Bricks of sillimanite, mullite, and silicon carbide are also satisfactory.

For smelting tin ores and for recovering tin from slags, etc., magnesite bricks and chromite bricks are suitable but expensive; for melting tin and its alloys, fireclay bricks are quite satisfactory, and for some alloys a cast-iron container will suffice.

For iron, iron alloys, and steels, the furnace roof may be built of bricks made of silica, fireclay rich in alumina or high-alumina bricks, but the lining is usually of magnesia, dolomite, or spinel. In some furnaces, the hearth is of basic material and the sides of fireclay (grog), or of silica bricks with a course of chrome bricks between. The use of unburned bricks (*above*) is increasing. Great care must be taken not to use bricks or other materials which react on each other. Thus, in a furnace constructed of silica or fireclay bricks with a lining of magnesia, a reaction will be set up between the two and the lining may fuse. If the magnesia is sufficiently thick its use may be satisfactory, but the thickness of an ordinary brick is seldom sufficient.

The *electrical conductivity* of refractory materials used in electric furnaces requires attention. Some materials are poor conductors when cold, but quite

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[1] Crucibles of fireclay, magnesia, alumina, thoria, etc., are still used in small electric furnaces.

[2] *Quality*, 1933, p. 18.

good ones when heated to redness. In fact, most refractory materials are fairly good conductors when at a high temperature. For this reason, electric furnaces should be designed in such a manner that the electric current does not pass through the portions of the furnace where it is not required.

A. F. Greaves Walker has suggested the use of the following refractory materials in electric furnaces for melting different materials:—

Metal.	Furnace Lining.
High-grade steels	Magnesia.
Ordinary steels	Silica.
Alloy steels	Magnesia.
Ferro-manganese	Magnesia or carbon.
Ferro-chrome	Magnesia or chromite.
Ferro-silicon	Silica.
Cast-iron (high temp.)	Silica.
,, (low temp.)	Fireclay.
Irons specially low in sulphur and phosphorus	Magnesia.
Copper (containing lead)	Magnesia.
,, (without lead)	Silica or magnesia.
Bearing metal	Magnesia low in silica.
Monel metal	Magnesia or silica.
Bronze	Silica or magnesia if the proportion of zinc is not too high.
Lead	Magnesia.
Silver	Silica.
Aluminium	Magnesia.

Enamel furnaces are of two kinds: (*a*) those used to melt a batch of materials so as to form a frit or enamel, which is afterwards ground and applied to the goods; and (*b*) those used for heating the goods after the enamel has been applied. For the former, reverberatory furnaces of the same kind as frit-kilns (p. 777) or rotary furnaces are used. Furnaces for producing an enamelled face on the goods consist of (i) a heat-generating chamber or furnace proper, (ii) the working space, and (iii) a general structure surrounding or enclosing both. For the combustion chamber, fireclay bricks with a refractoriness of Cone 34 to 35 are suitable for coal-, gas-, and oil-fired furnaces, though fused alumina bricks are better for the higher temperatures reached in some modern oil-fired enamelling furnaces.

The working space is usually the interior of a muffle (see p. 578). To ensure a good transfer of heat from the furnace to the working space, a material of high diffusivity (p. 372) is required, and silicon carbide bricks and slabs have many advantages in this respect, but are liable to oxidation, growth, and distortion under strongly oxidising conditions, particularly between 800° C. and 1000° C. In furnaces operating at somewhat lower temperatures, long service is frequently secured by the use of silicon carbide.

The use of high-temperature insulating bricks has led to rapid heating and fuel economy through decreased losses by radiation and heat-storage. The widest use of such bricks is possible in furnaces with clean gas or electrical heating, but with solid fuel it is necessary to protect the insulating bricks with an inner lining of bricks or slabs made of fireclay.

Fireplaces and fire-boxes require bricks which are sufficiently strong to resist the abrasion of the fuel and the pokers and other tools used in stoking.

The bricks must also be capable of resisting the sudden changes in temperature to which they are subject. Great refractoriness is seldom so requisite as resistance to abrasion, so that fireclay or grog bricks of medium quality and porosity are usually employed. These bricks soon become coated with a film of slag or clinker, which protects them from further abrasion and enables a more porous brick to be used than would otherwise be the case. (See also "Domestic fireplaces," p. 772.)

Forge furnaces are used for heating bars, etc., of metal to a red heat so as to render them soft enough to be hammered into the desired shape. Such furnaces are frequently heated in a very short time, and, consequently, there is considerable chance of the bricks spalling after many heatings, especially the bricks forming the roof, from which pieces tend to fall out.

There is also a possibility of the lining, especially at the bottom of the furnace, becoming coated with a basic slag consisting chiefly of iron and iron oxides derived from the scaling of the metal being heated in the furnace, and also from drops of molten metal produced by excessive superficial heating. This slag exerts a cutting action on the lining and also penetrates into the bricks and tends to hasten the spalling. For the roof of forge furnaces, therefore, it is necessary that the bricks should be rather coarse in texture and fairly porous so as to withstand the sudden changes in temperature which take place. They should have been well burned so as not to contract during service. Hand-made bricks are preferable for the roof, as they are more porous and less likely to spall than the denser machine-pressed bricks.

The bricks which form the bottom of the furnace need not be so resistant to sudden changes in temperature, but should be more resistant to corrosive and penetrating action of the scale and slag. Hence, for the bottom of the furnace denser bricks are preferable, the best being those with a fairly porous interior but a dense surface. Machine-made fireclay or grog bricks of No. 2 quality are generally found to be the most satisfactory for forges; there is seldom any need to incur the additional expense of using No. 1 bricks. Machine-made bricks fit more accurately, have a denser surface, and are more resistant to slag than hand-moulded bricks.

Foundry Furnaces.—The refractory materials used in foundries include those used in blast-furnaces (p. 754), cupolas (p. 770), and melting furnaces (p. 783), as well as in *casting pit appliances*, such as ladles (p. 781), stoppers, nozzles, and accessories (p. 550), crucibles (p. 583), and refractory cements (p. 723). Bricks suitable for these purposes have been described on the pages mentioned.

Frit kilns are used for melting the raw materials composing glazes and enamels. These substances are mixtures of bases and alkalies with silica, clay, borax, etc., in various proportions, and they have, consequently, a highly corrosive action on the brickwork of the furnace. The materials (or *batch*) are fed into the hot kiln and kept there until sufficient fusion has occurred, after which the fluid mass is run out through a tap-hole.

Frit kilns are of two kinds: (*a*) an oscillating (p. 784), or (*b*) a reverberatory furnace (p. 789) in which the materials are melted on a hearth.

A rotary fritting furnace is suitably lined with hard, dense fireclay bricks (grog bricks) or with a rammed lining composed of sillimanite, fused alumina, or silica, and a bond.

The *hearth* of a reverberatory frit kiln should be of grog bricks (Chapter II.), with very thin joints, the bricks having been made of a highly refractory material, graded so as to yield a close, dense product, the durability of which has been further increased by burning at Seger Cone 14 or above.

Underburned bricks of coarse texture are unsatisfactory for this kind of work, as they are more rapidly attacked by the frit than vitrified bricks.

The *arch* and upper parts of a frit kiln may advantageously be made of more porous bricks of equal refractoriness, but these bricks should have a dense " skin " or surface to prevent undue corrosion by the kiln gases.

The *bridge* of a frit kiln should be built of hard-burned, dense fireclay bricks containing at least 30 per cent. of alumina.

Galvanising furnaces are used to melt zinc and to contain it in the molten state whilst articles are immersed in it. The chief source of difficulty is the irregular heating caused by an alloy of zinc and iron (known as *dross*) which falls to the bottom of the container. A rise in temperature from 438° C. to 460° C. may treble the amount of dross. It is, therefore, customary to heat the cylindrical cast-iron container around the sides. The furnace is usually built of fireclay bricks, but a protective casing of 2-inch fireclay slabs is sometimes placed around the iron container. Troubles with galvanising furnaces are seldom due to the bricks, as zinc melts at 433° C. Silica bricks are not desirable, as they tend to spall.

Gas producers may be built satisfactorily of second quality fireclay bricks, unless the fuel is exceptionally high in ash, when harder-burned bricks will be necessary. The carbon monoxide gas is liable to decompose and deposit carbon in the pores of the bricks, causing them to flake, and the burning gas sometimes has a tendency to creep up the sides of the producer and so destroy porous bricks which are not hard-burned. These defects are largely due to defective design or inefficient management, so that they are not of great importance in the selection of firebricks. The lining of the producer immediately above the grate or rotary bottom may advantageously be made of grog bricks burned at Seger Cone 14 or above, the upper parts being made of cheaper firebricks, as the conditions are most severe from the grate or bottom of the producer to about 3 feet above it, on account of the slag-forming action of the ash and clinker in the fuel.

In large gas producers worked very intensively, the composition of the bricks should be adapted to the ash in the fuel, but a fairly large proportion of alumina is essential. Most fireclay and grog bricks have ample strength; they should have a fairly close texture and a fine skin on the face. The bricks in the hot zone should have a refractoriness equal to Seger Cones 32 to 34; bricks in the upper zones should have a refractoriness equal to Cones 30 to 32.

The bricks used for lining the dust-trap and gas-duct should be common firebricks, but care should be taken to use only those which have been well burned.

Gas-fired furnaces usually require better firebricks than coal-fired furnaces, especially for those parts where combustion occurs. This is due to the great penetrating power of the gases, the local intensity of the heat, and the absence of a protecting layer of soot. Apart from the combustion chamber, however, gas-fired kilns are more durable than those which are fired by coal, as the gases are more free from corrosive dust (ash), imperfect combustion, and varying temperatures.

The chief requisite in bricks for gas-fired furnaces is refractoriness, combined with sufficient hardness to resist the abrasion of the contents of the furnace. In the burners or combustion chambers, the bricks must be sufficiently dense to withstand the action of the gases and must be highly refractory, as the maximum temperature is reached at this part of the furnace. These two requirements are, to some extent, incompatible, and the best results are, therefore, obtained by using refractory grog or silica bricks which have been burned at Seger Cone 14 or above, for the burners. A somewhat cheaper brick may be used for the less strongly heated parts of the furnace.

Gas-works require refractory materials for the retorts (see pp. 667–675) and for the retort-settings (see p. 789).

Glass furnaces require bricks or blocks having the following properties:—

(i) Refractoriness equal to Seger Cone 27 or above.
(ii) Resistance to sudden changes in temperature.
(iii) Uniform corrodibility.

The last has not received the attention it deserves. For instance, it is unwise to use bricks made of a hard-fired grog with a more fusible clay, as the grog will produce " seeds " in the glass.

Siliceous materials often give good results and are sometimes preferable to grog, but the use of silica bricks in the lower parts of glass furnaces is fraught with some risk, as they are so readily attacked by glass, but, for the upper parts, silica bricks are preferable to those of fireclay on account of their tendency to expand rather than shrink when heated, and also because small pieces from silica bricks falling into the glass do less harm than those from grog bricks. The sides and bottom of a glass furnace are usually made of fireclay, as they require to be highly refractory, resistant to the chemical attack of the batch materials and gases, and to abrasion by both fused and unfused materials. The roof should usually be made of silica bricks.

Blocks are often preferred to bricks so as to avoid a large number of joints. The blocks are sometimes of fireclay and sometimes of Durham firestone, the former being preferable for parts in contact with the glass and the latter for other parts of the furnace. Various refractory materials suitable for glass manufacture are described on pp. 635–640. Recently, tank-blocks made of sillimanite and of fused alumina (see " Corhart Blocks," p. 512) have been found to be more durable than any others. The greatest corrosion in glasses made in tanks is at the level of the surface of the molten glass; far less corrosion occurs at a lower depth unless the bricks are made of very poor material. Consequently, when cheapness is a consideration, the best bricks should be used near the top of the tank, the next best for lining the tank, and any of the lower grade should be used for " backing purposes," where they will not come into contact with the glass.

At the fluid level, the best material available should be used in constructing the tank, carefully selected fireclay and grog, properly graded so as to produce a highly resistant material, or blocks of sillimanite and ball clay or of fused alumina. The blocks should be free from very coarse fragments of any kind, and particularly from those composed wholly of silica.

In many glass tank-furnaces the floor and the lower part of the sides are built of good grog bricks, which need not be of the very best quality, but the upper part of the tank should consist wholly of the best bricks.

The roof and the sides above the tank should be of silica bricks, because any " droppings " from such bricks will be dissolved in the glass much more readily and satisfactorily than those from bricks made of fireclay or other aluminous materials. For those parts of the structure not in contact with the glass, silica bricks are largely used. These bricks should not contain more than 2 to 5 per cent. of lime, 0·5 per cent. of magnesia, 1·5 per cent. of alumina, 1·4 per cent. of iron oxide, and 1 per cent. of soda and potash (together). The silica bricks should not contain more than 25 per cent. of quartz, nor less than 10 per cent. of tridymite and 30 per cent. of cristobalite, *i.e.* the specific gravity should not exceed 2·45.

Semi-silica bricks (p. 462) are used where constancy of volume is essential.

Stone blocks for the sides of the furnace must be set in their original bedding position, and those for the furnace bottoms should be perpendicular to this position (*i.e.* in both positions across the grain of the stone) so as to prevent spalling. For regenerator bricks see p. 785.

Gold- and silver-smelting furnaces are usually constructed of fireclay or silica bricks. When these metals are smelted with lead, the bricks should be more resistant to the lead slag. (See "Lead-working furnaces," p. 781, and "Cupelling furnaces," p. 770.)

Special care should be taken to use bricks which are accurate in shape, so that they may be laid with the thinnest possible joints, because any leakage through the joints may involve a serious loss of metal. The best jointing material is a mixture of potter's flint and fine fireclay made into a slip.

Some refiners prefer bricks which are low in alumina, as any gold and silver absorbed in them can be recovered more readily than from highly aluminous bricks.

Platinum, osmium, rhodium, and some other *precious metals* require the most highly refractory materials, and even then considerable difficulties are experienced (see pp. 582–631).

Cupelling furnaces—see p. 770.

Hearths are, strictly, the part of a furnace on which the material is heated, but the term is also applied to furnaces, some of which resemble a frit kiln and others a blast furnace. The action in a reverberatory hearth is less reducing than in a blast furnace, and, in some cases, it is oxidising. A hearth may, in fact, be used for a variety of purposes and with alternating conditions of oxidation and reduction. This type of furnace is cheap to build and is moderately economical in fuel. The bricks or blocks of which it is most suitably constructed are the same as those advised for the hearth of a frit kiln, reverberatory furnace, or blast furnace, according to the material to be treated.

Heat-treatment furnaces are used for annealing (p. 753) and for other forms of heat-treatment. The refractoriness demanded of the bricks is not high, but it is advisable to use hard, well-burned fireclay or grog bricks containing at least 30 per cent. of alumina where the conditions are most severe, and good firebricks for the remainder of the hot parts.

Insulating bricks between the interior and exterior and above the foundations are effective in saving fuel and in ensuring more uniform heating.

Kilns are used for burning bricks, pottery, cement, etc. Those used for cement must be capable of resisting the strongly corrosive action of this material, which is always rich in lime. (See Rotary Cement Kilns, p. 791.)

Other kilns must be built according to the temperatures to be reached. For building bricks, it is usually sufficient to use bricks of low-grade fireclay for the lining and for the crown of the kiln. The fire-holes should be built of bricks of better quality, to stand the abrasion of the tools used to remove clinker. For flash walls and bags, grog or fireclay bricks are best.

For *pottery*, the ovens must be lined with grog or fireclay bricks of moderate coarseness and high refractoriness, as the temperatures attained in some parts of the kiln may reach 1600° C. The conditions are not so severe as might be supposed, and, except in the fireplaces and bags, little difficulty is experienced in obtaining suitable bricks, especially if these have been burned at the finishing temperature of the kiln in which they are used.

For *firebricks*, the kilns should be lined with grog or silica bricks of high refractoriness which have been burned at or above any temperature they will reach when in use. This is particularly necessary in the upper part of the kiln, as great shrinkage there might result in the collapse of the kiln. Silica bricks collapse more suddenly than those made of grog and are correspondingly less suitable.

Ladles.—The refractory materials used for lining the ladles into which molten steel runs from the furnace must necessarily vary according to the steel for which it is used. In some cases, an acid-resisting lining is necessary, whilst in others, a basic lining must be employed. The nozzles and stoppers of ladles must also be made of carefully selected materials in order that they may have a maximum of durability and efficiency. The molten metal tends to enter the refractory material by capillary action, and then acts as an extremely powerful reducing agent and very quickly disintegrates the ladle, nozzle, or stopper.

Silica bricks are largely used, but A. Reynolds has stated that the production and retention of perfect steel is impossible if it comes into contact with any material which is neither neutral nor basic. A further objection to acid linings for ladles, etc., is that if they become covered with manganese monosilicate, which is rapidly oxidised as the ladle is emptied, the manganese and iron oxides thus produced will spoil the next lot of steel poured into the ladle.

For further information on lining ladles for steel casting, see p. 549 *et seq.*

For the linings of ladles for molten iron, bricks, or blocks made of a tough, plastic clay, composed of about 54 per cent. of silica, 30 to 35 per cent. of alumina, 10 to 12 per cent. of combined water, and 3 to 4 per cent. of ferric oxide are sufficiently refractory.

Ladles for mild steel and copper may be lined with similar bricks, which are protected by a coating of tamped fireclay.

The porosity of the lining material should not exceed 18 per cent. by weight (of water absorbed) and the use of a fairly large proportion of coarse grog is often advantageous.[1]

A low after-contraction and high resistance to slag are both important, and on no account should bricks with dark cores be used.

Lead-working furnaces are of three chief types, viz. roasting, smelting, and refining furnaces.

The temperature attained in roasting lead is not high, so that if the portion of the hearth next to the fire-bridge is made of first-class firebricks, the remainder of the furnace may be made of second-grade firebricks. If the charge contains more than 35 per cent. of lead, it may corrode the lining unduly. This should be prevented by keeping the proportion of lead below this figure, *e.g.* by adding silica to the charge.

In lead-smelting furnaces, the slags are basic, so that the lining should also be basic, and though they are usually of fireclay, it is far better to use magnesia, bauxite, or chromite bricks. A mixture of equal parts of magnesia and chromite bricks ground to a coarse powder, reformed into bricks and burned at 1500° C., has proved particularly durable.

The liquating hearths used for separating lead and copper may be built of second-class firebricks, but magnesia is preferable, being much more durable.

The reverberatory furnaces used for lead smelting work at so low a temperature, that good fireclay bricks are amply resistant for the lining, and for the exterior brickwork good building bricks may be used. The hearth is usually "prepared" and made slag-tight by melting a mixture of litharge and clay on it, prior to filling the furnace (see also "Smelting Furnaces," p. 793). Lead slags are so mobile and so penetrating that the joints between the bricks must be as thin as possible, or the loss of lead will be very serious.

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[1] A. T. Green, *Trans. Cer. Soc.*, 1928, **27**, 84.

For simply melting lead and lead alloys, *e.g.* in an electrically operated furnace, no refractory container is needed, as one made of cast-iron or a nickel-chromium-iron alloy is quite satisfactory, requires less current and is stronger.

Lime Kilns.—Lime kilns require a particularly good quality of firebrick because the lime itself has noticeable action on the bricks in two ways: it attacks them chemically and rubs against them in its descent through the kiln, until it gradually wears them away mechanically. As the linings of continuous lime kilns are maintained at a high temperature for a long time it is necessary that the firebricks used should be of a highly refractory nature.

There are several different types of lime kilns in use, and, as many lime burners are using kilns which have been modified in accordance with their own ideas, it is not surprising that firebricks which have proved highly satisfactory in one works or area have been condemned as useless in another. The temperature reached inside a lime kiln seldom exceeds 1200° C.,[1] though 1450° C. is sometimes reached in the hottest zone. One great difficulty in selecting bricks is that they are attacked chemically by the lime and so present the appearance of having been heated excessively, whereas in reality the temperature has not been excessive. The pressure of the lime in contact with the bricks can reduce their resistance, and even a small rise in temperature above 1100° C. can greatly increase the destruction of bricks by lime.

In mixed-feed shaft-kilns, the greatest wear is in the hot zone, which is usually the middle half of the total height of the kiln, so that the most resistant bricks should be used there. In the upper and lower quarters of the height of the kiln, No. 2 grade fireclay bricks are usually quite satisfactory.

In externally fired kilns, the chief wear is in the arches over the fireplaces, as the highest temperature is there associated with reducing gases. In Hoffmann kilns, the chief wear and tear is in the crown and is due solely to the heat, as the lime does not touch this part of the structure.

The most generally suitable bricks for lime kilns are those made of fireclay and grog. For the hottest zone of a vertical kiln they should have a refractoriness equal to Seger Cone 32 to 34 and contain at least 38 per cent. of alumina. For the other zones and for general use in Hoffmann kilns, fireclay bricks with a refractoriness equal to Seger Cone 28 to 32 and containing 30 per cent. or more alumina are usually satisfactory.

Bricks made of bauxite, fused alumina (e.g. *Dynamidon bricks* or the like) are good, but are considered to be too expensive. Magnesia bricks tend to be weak and too easily worn away, but if sufficiently hard they are very durable apart from their tendency to spall. Spinel bricks are too expensive, but otherwise are satisfactory.

Silica bricks are too readily attacked by lime, though in some cases they are quite satisfactory.

The fact that lime readily combines with silica and alumina at high temperatures does not prevent the use of these materials or of fireclay bricks for lining lime kilns. The temperature at which combination can occur is only attained in a small part of the kiln, and if the bricks are accurate in shape and have very thin joints the severity of the attack will be low. If, on the contrary, the bricks are rough, inaccurate in shape and are laid with thick joints, the facilities for their destruction by lime are greatly increased. Large blocks, such as are used in blast furnaces, are more expensive.

Firebricks in lime kilns must be able to resist sudden changes in temperature.

Highly vitrified and dense bricks should be avoided, but the faces should

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[1] 900° C. to 1000° C. is usual.

be close in order to resist the action of the lime as long as possible. Soft, porous-faced bricks are quite useless, no matter how heat-resisting may be the clay from which they are made; they are too rapidly attacked by the lime particles, which eat into their substance and bring about an early fusion. The usual mistake is to use firebricks which have too much raw clay in the material from which they are made, and the result is bricks lacking in strength because the ingredients are not properly proportioned. It is well known that a No. 2 grade of firebrick may, by reason of its greater hardness and strength, prove to be a better brick for withstanding the abrasive action of the lime than a more refractory but softer brick. A second-grade brick has usually the further advantage of a smoother face, and the greater closeness of this prevents the action of the lime from being so intense. Highly aluminous fireclay bricks are superior to more siliceous ones, and have a greater resistance to abrasion and corrosion.

Insulating bricks (p. 395) should be used between the interior and exterior of the kilns. Many complaints of the behaviour of bricks in lime kilns are not due to faults in the bricks, but in the design, construction, or management of the kiln.

Lye calciners consist of a pan of refractory material heated by a furnace beneath. The bricks or tiles used for the pan must be highly aluminous, so as to present a maximum resistance to the action of soda. Bauxite bricks (Chapter V.) or highly aluminous grog bricks (Chapter II.) are suitable for this purpose. They must be hard-burned, have a close texture and be laid with the thinnest possible joints.

Malleable-iron furnaces are subject to sudden changes in temperature, and so they should be lined with fireclay bricks having a fairly dense skin so as to resist corrosion, but a porous body. No. 2 grade firebricks are usually satisfactory, as the temperature attained seldom exceeds 1350° C. Basic bricks are not needed, and high-alumina bricks are needlessly expensive.

Silicon carbide bricks have given satisfactory results, but require a backing of insulating bricks to neutralise their high thermal conductivity (see also "Cupola Furnaces").

Melting furnaces are used for fusing various substances—chiefly metals and alloys, but they are also used for melting enamels, frits, and other materials. The chief melting furnaces are *cupola furnaces*, *air furnaces*, *reverberatory furnaces*, *crucible furnaces*, *rotary furnaces*, and *electric furnaces* (p. 772); with the exception of the last two, all these furnaces have been in use for many years.

Muffle furnaces are furnaces with an internal vessel or muffle made of refractory material. Fireclay or grog bricks should be used for the casing around the muffle; they should be of high refractoriness, moderate porosity, and should be burned sufficiently hard not to change their volume when in use. The muffle should be made as described in Chapter XI.

Nickel-working Furnaces.—As nickel melts at about 1470° C. the furnaces in which it is reduced or melted should be lined with high-alumina bricks, No. 1 grade fireclay bricks, or silica bricks. Some nickel alloys melt at much lower temperatures.

Oil-fired furnaces require much better firebricks than those using coal as a fuel, as the temperature of the flame is considerably higher, so that unless the lining bricks are of the best quality they will deteriorate rapidly in use, especially if the burners are not skilfully managed. Where the firing is carelessly carried out, the flame will "cut" the bricks if they are of unsuitable quality. Another difficulty which may occur is the decomposition of hydrocarbon gases, and the deposited carbon exerts a catalytic action in the clay which affects the rupture of the pores of the brick and thus brings about their destruction. Spalling may also occur if unsuitable bricks are used and the heating is very rapid.

The most suitable bricks for oil-fired furnaces are fireclay or grog bricks of good quality. Silica bricks are too liable to spall, and other refractory bricks are generally too expensive for this purpose.

To avoid spalling it is necessary to use bricks of a porous and moderately coarse texture, though excessively porous bricks are undesirable, as they may be unduly attacked by any carbon which may be deposited upon them.

It is important that the bricks should be uniform in texture in order that they may be able to resist the sudden changes in temperature which may occur.

A high refractoriness is also necessary, the bricks needing to be considerably more refractory than the highest temperature to which they are likely to be exposed during use.

A good shape and uniformity in size are necessary in order that the bricks may be laid in the thinnest possible joints. It is generally desirable to put a few loose bricks into the furnace at the point where the flame may play on the walls of the combustion chamber. These may be replaced when eaten away badly, and they serve to protect the lining, which is less readily replaced.

In some oil-fired furnaces, the most durable bricks are those made of fireclay in which the alumina does not exceed 36 per cent. As oil-fired furnaces are usually heated very rapidly, the bricks should contain a large proportion of grog, which should be coarse. Bricks which tend to spall are useless for such furnaces. The arches may be built of semi-silica bricks or of bricks made of siliceous fireclay.

Open-hearth furnaces are described on p. 794 under " Steel Furnaces."

Oscillating furnaces do not rotate completely, but only sufficiently to permit them to discharge their contents—see " Melting Furnaces " (p. 783).

Ovens for potters are described under *kilns* (p 780). For bakers' ovens second-grade firebricks are usually satisfactory, as the temperature reached is not very high. Bricks suitable for boilers and fireplaces are quite satisfactory for bakers' ovens.

Powdered Fuel Furnaces.—Furnaces in which *pulverised fuel* is burned require special bricks to be used where molten ash in the form of "dust" impinges on the interior of the furnace. Dense, hard-burned fireclay (grog) bricks are usually best; they should contain at least 38 per cent. of alumina. Sillimanite and other high-alumina bricks are also satisfactory, but expensive. Chromite bricks have not given satisfaction because they react with any iron in the ash. In some furnaces the conditions are so severe that no known refractory material can withstand them unless some form of cooling is applied, and in these cases water-cooled linings are used.

Puddling furnaces are of the reverberatory type. The hearth may be made of magnesia bricks with a covering of slag. The sides should be built of magnesia bricks up to a short distance above the surface of the bath. The remainder of the sides and the roof should be of silica or fireclay bricks.

In **refuse destructors,** the maximum temperature attained is not extremely high, though it must be sufficient to secure the ignition of the combustible matter. The chief factor in these furnaces is the supply of sufficient hot air, the heat for which must be supplied regeneratively. The use of grog bricks is found to be quite satisfactory and, in some cases, bricks made exclusively of fireclay are all that can be desired. The bricks should be strong rather than highly refractory, as the chief cause of their destruction is abrasion.

Recuperators consist essentially of a series of flues surrounded by other flues; air is passed through one set and is heated indirectly by hot gases passing through the other set of flues. Sometimes tubes form the inner set of flues, and in some recuperators the sets of flues are arranged side by side instead of concentrically. It is usually important that no gas should leak into the air-passages, so that the joints in the latter should be as thin and as gas-tight as possible.

The portions of a recuperator which keep the air separate from the hot gases should, theoretically, be built of material of high thermal conductivity, so that silicon carbide offers special advantages, but in most recuperators fireclay pipes, tiles, or bricks are used, with silica as an alternative material. For the remainder of the structure, fireclay bricks, grog bricks, and silica bricks are chiefly used.

Bricks for recuperators should be capable of being used continuously at a working temperature of 1200° C.; they must have ordinary mechanical strength (80 to 120 tons per square foot) and be insensitive to sudden changes in temperature and resistant to both steam and flue-dust. They must be accurate in shape and size, so as to be capable of being laid with very thin joints, and should have as smooth a surface as practicable.

Flue-dust is a constant source of trouble, as it tends to corrode the structure; to minimise its action, recuperators should be built of fireclay (grog) bricks, blocks, pipes, or tiles, or silica bricks. Some flue-dust is basic, but basic bricks can seldom be used in recuperators.

High-alumina bricks and sillimanite bricks are excellent, but are commonly thought to be too expensive.

Other properties required in the bricks, etc., used for recuperators are also required in those used for regenerators (*q.v.*), though recuperators are not subject to the frequent and sudden changes in temperature which occur in regenerators.

In the type of recuperators known as *Cowper stoves*, blocks of a special shape (p. 541) are used. Those in the lower part of the stove must have ample mechanical strength at the highest temperature to which they attain when in use, at least 20 per cent. of alumina and a refractoriness not less than Seger Cone 30. For the middle and upper parts of the stove rather more refractory blocks are desirable as the temperature is higher, and it is usual to employ fireclay blocks containing 30 per cent. or more of alumina and having a refractoriness not less than Seger Cone 33.

The blocks must be accurate in shape so as to fit well together, presenting a minimum of unnecessary resistance to air and gases and yet having the smallest possible tendency to leak. The individual blocks should have the same properties as bricks used for filling regenerators.

Regenerators consist of a brickwork chamber filled with bricks or other units, arranged in *checkers*, *i.e.* with spaces between them, so as to permit the ready passage of air or other gases. They are worked in pairs, one being heated for several minutes by passing hot gases through it, after which a reversing valve is operated so that the second regenerator is heated by the hot gases, and air is heated by being drawn through the first regenerator. The reversals are made every 10 to 15 minutes, or oftener if required.

Bricks for regenerators are often known as *checker-bricks*; they should have the following characteristics:—

(1) Sufficient *refractoriness* to stand the highest temperature reached.

This is not difficult to secure, the chief cause of low durability being the decomposition of the bricks by gases, dust, etc., and not to their being insufficiently refractory (see *Abrasion*, p. 749).

(2) *Resistance to the chemical action* of the hot gases and the dust therein on the bond of the bricks, whereby the latter is destroyed, leaving the bricks friable, weak, and liable to flake. This is best secured by burning the bricks at a temperature corresponding to Seger Cone 14 or above. Basic bricks are preferable to the fireclay or grog bricks generally used, but are regarded as too costly. The dust in the gases is usually of a basic character, and therefore specially active in attacking siliceous or porous fireclay bricks. Whiteley and Hallimond have found that the main cause of corrosion is the metallic oxide which accumulates in the regenerators, the material being carried over by the gases either as suspended particles or as vapour, chiefly during the "boil" and not between the melting and boiling as hitherto surmised. The suspended matter consists chiefly of liquid drops which settle on the bricks and result in a partial fusion of the surface of the bricks. This action can only be avoided by making the bricks as neutral as possible, or by using magnesia or other basic bricks, and these are usually too sensitive to sudden changes of temperature. It is most important that the regenerators should be cleaned out at sufficiently frequent intervals (usually every fifteen to twenty weeks), as they are liable to become clogged with dust.

Where the dust is not important, silica bricks have sometimes been found satisfactory, though their sensitiveness to sudden changes in temperature is against their extended use in regenerators. Checker-work made of silica bricks does not choke so readily as that of clay, as any sooty deposit does not so readily penetrate silica bricks. Whilst silica bricks are largely used in the construction of the checker-work in acid open-hearth furnaces, their use for other regenerators is worth further consideration by engineers.

In some cases, the checker-work of regenerators is made partly of fireclay and partly of silica bricks, the latter being confined to the top of the regenerator, as the fluctuations of temperature nearer the bottom may be too great for the silica bricks to withstand. The temperature at the top varies from 700° C. to 1300° C., whilst at the bottom it is considerably lower, 450° C. to 800° C., though in some cases it may rise to nearly 1300° C. Whilst it is inadvisable to run any risks of silica bricks failing on account of fluctuations in temperature, it is desirable to use as many of these bricks as possible in the checker-work, on account of their greater conductivity, which increases the heating capacity of the regenerator. The strength of the bricks used in the checker-work is not so important as in the walls, and, provided allowance is made for the expansion of the bricks, they need only be moderately hard-fired.

(3) *Insensitiveness to Sudden Changes in Temperature.*—This is best secured by using porous bricks which have been burned very hard and have a dense "skin" or surface to resist the chemical action of the hot gases. This insensitiveness is very important in bricks used for the checker-work in regenerators and in all parts of stoves which are liable to the sudden inrush of cold air on to the hot brickwork. Highly porous bricks are sometimes advantageous for such checker-work, as they absorb the fused material more readily and do not choke so easily as dense bricks. In checker-work used only for the passage of air, hard, compact bricks which are good conductors and capable of resisting high temperatures are preferable.

(4) *High thermal conductivity*, so that the stove may transfer the heat from the gases to the air as efficiently as possible. For the highest thermal conductivity, a close-textured material is essential.

(5) *Mechanical strength* to resist the crushing action of the superimposed brickwork at the temperatures at which the bricks are used. In some instances, the load on the bricks is very great, thus necessitating a highly refractory brick with great mechanical strength.

(6) *Low coefficient of expansion*, as large changes in volume cause rapid disintegration.

Ample allowance must be made for the expansion of the bricks when heated, and to keep this at a minimum only those bricks which have been specially well burned should be used.

It is important that all bricks used in the construction and repair of a stove should be from the same works and of the same character; bricks from different sources often react on each other to their mutual detriment.

Regenerative air-furnaces, on account of the high temperature attained and their intermittent action, are particularly severe on firebricks. It is necessary to select the bricks with great care, or they will not withstand such trying conditions.

All the bricks should be hard-burned so that they undergo no further shrinkage in use, and, usually, bricks which have been fired below Seger Cone 14 should be rejected.

The foundation of regenerators usually consists of a concrete platform with several courses of firebricks above it. These need not be particularly refractory, as they are seldom likely to attain a temperature of more than 600° C. to 700° C. They must, however, be of uniform size and capable of bearing a great load.

The foundation walls are usually composed of silica bricks, which must be capable of withstanding a great load, though the refractoriness required is not great. The bricks must be uniform in size (varying not more than $\frac{1}{16}$ inch per foot for bricks less than 12 inches long and $\frac{1}{8}$ inch per foot for blocks larger than this size), and laid with the thinnest possible joints. The permanent expansion must be as low as possible to prevent the " in-creeping " of the brickwork. The advantage of silica bricks for this part of the structure is that they do not shrink continuously under a steadily applied load, as do fireclay bricks.

For the side walls, close-grained grog or fireclay bricks (Chapter II.) should be used, similar bricks of coarser grain being used for the roofs. The lower part of the side walls may advantageously be made of chromite or magnesia bricks, as these offer a greater resistance to the slag, but such bricks are costly and, unless very carefully made, they spall and crack on account of the great and oft-repeated variations in temperature.

The flues connected with the regenerators should be lined with fireclay bricks, but may be backed by silica bricks, the former being necessary on account of the fluctuations in temperature. A high refractoriness is not necessary in most cases.

The sole flue is generally built of hard-fired silica shapes, as this must withstand a higher temperature.

For the checker-work, or " filling," fireclay (grog) bricks are usually the most suitable, but it is important that the iron compounds present should be small in amount and very uniformly distributed, so as to minimise the deposition of carbon in the spaces between the bricks.[1]

Silicon carbide and plumbago bricks are, theoretically, best on account of their high thermal conductivity, but in practice their disadvantages outweigh this property.

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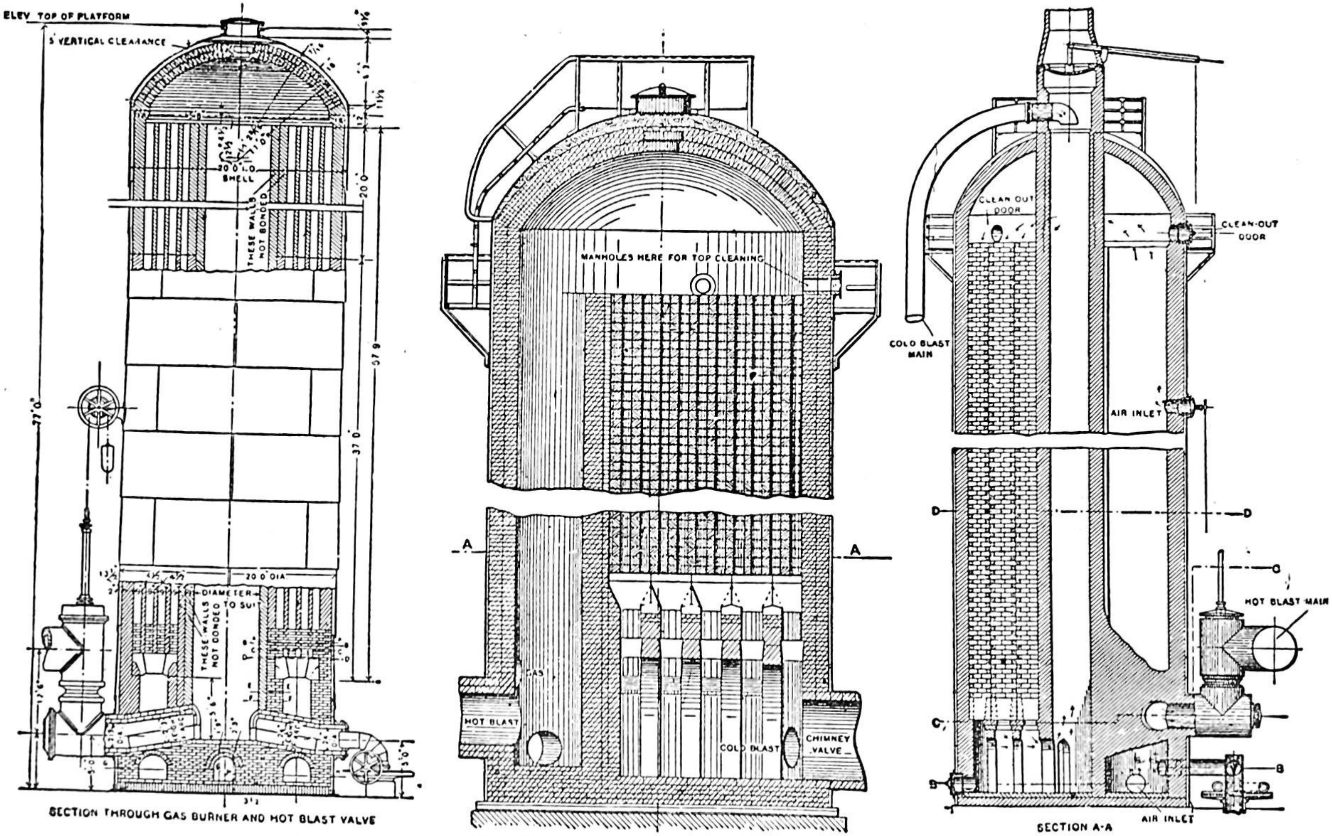
[1] The dust which accumulates is largely iron oxide, not slag.


SECTION THROUGH GAS BURNER AND HOT BLAST VALVE

SECTION A-A

FIG. 170.—Stoves for heating air-blast.

The porosity of regenerator bricks does not seriously affect their efficiency as heat-transferrers, but it does increase their resistance to rapid changes in temperature.

At regular intervals the bricks in a regenerator should be removed and cleaned, and the bad ones replaced. Those which have become glazed during use are not satisfactory and should not be used again, but clean, unglazed bricks are quite satisfactory, especially in the lower part of the checkers.

Reheating furnaces (see *Annealing Furnaces*).

Retort settings are the furnaces used to heat retorts, and afford a good example of the various demands refractory materials have to satisfy. The arches and walls of the combustion chamber must withstand the highest temperature of the gas and flames, so that the principal requirement for this part of the setting is high refractoriness. No considerable changes of temperature occur during the working of the setting, so that porous bricks may be used.

Bricks made of Ewell sand are often used to advantage for fitting retorts into the division walls of the setting. The division walls need not be highly refractory, as in properly designed settings they are not in direct contact with the flame. They should have great mechanical strength, as they have to bear the whole of the superstructure, and are preferably made of hard-burned fireclay or grog bricks, but a general practice is to use silica bricks inside the main arches and above the producer level, and fireclay bricks for the remainder of the setting. The silica bricks should have no serious permanent contraction or expansion when in use and should, as far as practicable, be free from unavoidable thermal expansion, which should not exceed 2 per cent. linear and for which allowance should be made.

The use of insulating bricks (p. 395) for retaining the heat in the setting is increasing. Most of these bricks need to be protected from the most intense heat by a lining of refractory bricks.

The outer walls of the setting are usually built of fireclay bricks, but building bricks, made by the stiff-plastic process, of high porosity and low thermal conductivity are preferable, as they lessen the losses by radiation.

The materials used for retorts are described in Chapter XIV.

The producer should be lined with bricks of the kind described under "Gas Producers" on p. 778.

For information on settings for retorts for distilling zinc, see "Zinc Furnaces," p. 798.

Reverberatory furnaces are used for roasting or smelting ores, heating metals, chemicals, etc. They consist of a lengthy basin or hearth surmounted by an arch and having a fireplace at one end and a chimney at the other. The flames and hot gases from the fireplace pass over the hearth and below the arch and thence to the chimney, striking the arch first and being deflected on to the hearth. Hence, the hearth, arch, and fireplace must be of refractory bricks. The conditions inside the furnace may be either oxidising or reducing according to its use; this must be considered when ordering the bricks.

The *hearth* must be made of bricks which will withstand the corrosive action of the ore, slag, or other substance heated upon it, and these bricks must, therefore, be of fireclay, grog, or aluminous (bauxitic) or basic material, according to the nature of the charge, powerful bases requiring a basic or aluminous hearth, whilst for acid or neutral substances a fireclay, grog, silica, or slag hearth is preferable (see *Frit kilns* and *Hearths*, also *Copper furnaces*, *Steel furnaces*, etc.). The bricks should have a close texture, be hard-burned and of great refractoriness, and they should be accurate in shape so as to be laid with the thinnest possible joints. The hearths of reverberatory furnaces are sometimes covered with sand, crushed rock or other material of a suitable nature. Such a lining must, of course, have the same capacity for resisting corrosion as the bricks used in other parts of the furnaces. In Swansea, sand from the seashore is used for this purpose, as the bases in it are sufficient to cause the partial fusion of the sand. Where quartzite is employed, as in America, it is necessary to add a fluxing agent, such as felspar. The chief disadvantage of some sand is that it absorbs too much metal, which cannot be recovered economically. Where such a loss occurs it is generally preferable to line the hearth with bricks, and not loose sand cemented by some fluxing material.

Where the materials to be heated in the furnace are, or tend to be, basic in character, bricks made of fireclay, grog, or silica are useless and a basic brick made of magnesite or bauxite must be employed. Thus, magnesia bricks are used in the basic open-hearth furnaces employed for steel-making provided they do not contain more than 12 per cent. of silica. The chief difficulty experienced with magnesia bricks is that they are unduly sensitive to sudden changes of temperature and tend to spall during use. This difficulty has, however, been obviated to some extent by the use of " metalkase " bricks and spinel bricks. Magnesia bricks are found to be most satisfactory in softening and cupelling furnaces for lead and silver; they are also largely used in copper, antimony, and arsenic furnaces. The hearths of puddling furnaces are generally lined with magnesia bricks to a short distance over the highest level reached by the molten metal.

Chromite bricks and carbon bricks have also been used to some extent for copper-working furnaces, carbon bricks being especially useful for lining the matte tap-holes. Chromite bricks have the advantage over magnesia bricks for copper smelting, in that they do not crack and spall readily and are more resistant to corrosion. They have, however, an important disadvantage, as they absorb too much molten metal. One firm has reduced the loss from this by grinding up old chromite bricks, extracting the useful metal and making new chromite bricks from the residue.

The *sides and arches* of reverberatory furnaces are not called upon to be so resistant to slags and corrosive substances as the bricks which form or line the hearth, but the side and arch bricks must be resistant to the gases and flue-dust generated in the furnace, and also be as constant as possible in volume, for if they contract when in use they may fall out and contaminate the molten bath, as well as endanger the stability of the furnace. The most suitable bricks for the sides and arches of reverberatory furnaces are those made of fireclay or silica, and these are generally employed. Some firms prefer fireclay bricks for the sides and silica bricks for the roof; others prefer to use silica bricks throughout. These bricks should be thoroughly well burned and should have a texture similar to that of the hearth bricks, as this enables them to resist abrasion, as well as chemical action. The latter is, in some cases, quite serious and must be particularly guarded against where the flue-dust is highly charged with volatilised oxides.

The *ports* of open-hearth steel-furnaces should be composed of bricks specially resistant to corrosion, as the cutting action of the flame is very intense and furrows soon appear, even in bricks of the best quality. The abrasive action of the fine dust from the producer gas shows its mark along the side-walls of the furnace. Silica bricks withstand the severe conditions to which the greater part of the brickwork is exposed as well as any bricks yet tried, provided they do not contain more than 5 per cent. of impurity, including 1½ to 2 per cent. of lime used in binding the bricks. Alkalies in the form of silicates are undesirable, but less harmful than alkaline oxides.

The *fireplace* should be built of first-class fireclay or grog bricks, of sufficient refractoriness to resist any temperature which may be attained during the firing of the furnaces. Provided bricks of good quality are used and they are of suitable shape and size and have been well burned, so as not to contract in use, little difficulty should be experienced with the fireplace lining.

Where a *bridge* is employed in the reverberatory furnace, it should be composed of first-class fireclay, grog or silica bricks of accurate shape and size, with a dense surface and an open-texture interior, so as to resist the high temperature attained and the abrasive action of the dust from the burning fuel, which is carried over with the hot gases.

The conditions in many reverberatory furnaces are so severe that too much care cannot be taken in ascertaining, as precisely as possible, the requirements in each part of the furnace, and then selecting, for that part, bricks of a suitable chemical composition and physical texture. By considering each part of the furnace separately and meeting its requirements as accurately as possible, a long life for the bricks will be ensured so far as the manufacturer is concerned. In addition to these precautions, it is necessary that the furnace should be suitably designed and that it should be worked in a skilful manner.

Most of the complaints against firebricks in reverberatory furnaces are due to: (i) the selection of bricks of an unsuitable nature for the particular part of the furnace in which they are employed, though they may be quite satisfactory in other parts, (ii) the use of badly shaped bricks laid with thick joints, (iii) faults in the design of the furnace and (iv) careless or unskilled management of the furnace.

Some furnaces are described as reverberatory, although they consist of a simple horizontal cylinder lined with refractory material; they are misnamed (as there is little or no reverberatory action on the flames), and would be better described as open-flame furnaces; when they rotate they are known as rotary furnaces (p. 793).

Roasting furnaces are usually of four types: (*a*) hand-stirred reverberatory furnaces (*q.v.*), (*b*) rotary cylinders (*q.v.*), (*c*) muffles (*q.v.*), and (*d*) circular multiple-hearths over which the material is moved by stirrers, so that it passes over each hearth in turn. In furnaces of the (*d*) type, the greatest wear occurs in the stirrers; in all roasting furnaces, the brickwork is chiefly worn by abrasion, but the process is usually so slow as to be negligible. (See also *Copper-working furnaces, Lead-working furnaces*, etc.)

Rotary cement kilns (fig. 33) consist of a cylinder about 60 feet in length and 6 feet or more in diameter, which is slowly rotated about its axis by simple gearing. The cement-slurry enters at one end and passes out at the other; the fuel enters at the lower end and consists of coal-dust carried by a blast of air which is more than sufficient for its combustion. The warming zone makes no great demands on the furnace lining, provided it is sufficiently resistant to the abrasion of the cement mix as it falls into the kiln and then acquires a rotary motion. This zone does not, therefore, need a highly refractory lining.

The second or fluxing zone is the one in which the maximum temperature is reached and, consequently, is the one in which the conditions are most severe. Experience has shown that the lining of this zone should be made of highly aluminous material, as this offers the greatest resistance to the action of the cement. The cement is very rich in lime and so exerts a highly corrosive action on the refractory lining, unless it is made of a basic or aluminous material. At one time, it was extremely difficult to obtain bricks which would produce a satisfactory lining on account of the widespread belief that silica bricks are more refractory than those made of grog or fireclay, so that the latter were not given much attention. In reality, aluminous (clay) bricks are far less readily attacked than those made of almost pure silica. The Continental brick manufacturers soon realised the superiority of alumina over silica with respect to bases, and most Continental rotary kilns are, therefore, lined with aluminous bricks of the bauxite type and consisting of fireclay to which 20 per cent. or more of bauxite has been added (see Chapter V.), so as to produce bricks containing about equal parts of silica and alumina. Well-vitrified fireclay bricks, when sufficiently refractory, have proved excellent, and usually last six to nine months in the hottest zones of the kiln. They should contain not less than 35 per cent. of alumina and have a refractoriness equal to that of Seger Cone 32. In Great Britain the earliest rotary cement-kilns were lined with clinker blocks, but these were not durable. Fireclay bricks were tried and serve well, except for the hottest zone (24 to 36 feet). Bauxite and other high-alumina bricks appear to be the most durable and are now increasingly used.

The alumina must be combined with any clay present; it is not sufficient to add bauxite to fireclay merely to increase the alumina-content; the firing of the bricks must be at least to 1500° C. Mullite bricks and "sillimanite" bricks are satisfactory, but are liable to spall. Recently, it has been found that bricks of fused alumina of the Corhart type are extraordinarily durable in cement-kilns.

Hand-made bricks, if well shaped, are better than machine-made bricks, but badly shaped bricks are not suitable for rotary kilns.

Spalling is sometimes caused by the inner face of the bricks becoming vitrified and so possessing a different degree of elasticity from the remainder of the bricks. This difference sets up stresses which result in the vitrified portions breaking away.

To prevent undue loss of heat, a ring of porous insulating bricks should surround the lining of the hottest zone. Bricks made of fused alumina appear to be very satisfactory for lining the hottest zone in a rotary kiln, as they are highly refractory, highly resistant to chemical action, and are remarkably constant in volume. As, however, such bricks are very expensive to manufacture, they are seldom employed, though fused alumina may be used as a grouting over an ordinary fireclay lining.

As an alternative to a brick lining in this part of the kiln, a pasty mixture of raw and burned cement may be used. Another method of forming a protection for the firebricks is to cover them with a coating of cement-clinker. The firebrick lining is first covered with a layer of salt, and, after raising the temperature of the furnace to the sintering-point, a charge of clinker is admitted. This reacts with the salt and silica of the firebricks, a glass being formed which welds the clinker and bricks together, and the former is then well beaten into place. In this way, it has been found that a firebrick lining will last for years, though it is necessary to repair the clinker coating from day to day. When the rotary kiln is stopped for any purpose, this coating invariably falls off upon cooling, and the same operation, with or without the use of salt, proceeds each time the kiln is re-lighted.

Rotary kilns of smaller dimensions are also used for roasting ores, etc. The refractory bricks or blocks used for lining them must be made of materials corresponding to the charge in the furnace, a basic charge requiring a basic lining, and so on.

Magnesia bricks are too sensitive to sudden changes in temperature to be useful in rotary kilns, and they are unsuitable, as they tend to increase the proportion of magnesia in the cement. Chromite bricks are far too costly to be practicable, but chrome-magnesia bricks are very resistant to cement clinker and are sometimes cheaper than high-alumina bricks. In Canada, dolomite-chrome bricks, containing about 7 per cent. of chromic oxide and sufficient silica to form 20 per cent. of dicalcium silicate with the lime, have been found to be superior to high-alumina bricks.

Carbon bricks cannot be used, as they burn away and are liable to spoil the cement. Silica and carborundum bricks are destroyed so quickly by the cement that they are useless.

There is no need to import bricks for lining cement-kilns, as British manufacturers are now producing excellent bricks for this purpose—equal to any made abroad—and continued improvements may be expected.

The bricks should be made to fit the radius of the kiln and put in dry without any cement. The last brick in the circle, being the key, should be well driven and the whole of the lining should be finished with a grouting of neat cement, care being taken to fill all the interstices.

If the kiln is not entirely stable, especially at the roller-bearing rings and girth-gear, the lining will give trouble.

In the cooling zone of the kiln, it is important to use refractory bricks which are not sensitive to sudden changes of temperature. Fireclay and grog bricks of good quality and rich in alumina are the best, provided they are sufficiently compact and hard to resist the corrosive and abrasive action of cement clinker, yet not so glassy as to be spalled by currents of cold air impinging on them.

Rotary furnaces, for melting metals and alloys, preparing frits and enamels and for heating other substances, consist of a steel cylinder mounted horizontally on trunnions or on rollers and capable of slow rotation. The cylinder should be lined with bricks of a nature which should correspond to the contents or charge; some furnaces are lined with a rammed lining throughout, whilst others have rammed material inside the brick-lining. For melting iron and steel, the lining is commonly of silica; for brass and bronze, fireclay and grog bricks or a mixture of fireclay and grog are preferable. For copper refining, a siliceous lining is used, but for aluminium special refractory materials are employed (see under the various metals in the present chapter).

Smelting furnaces are usually either of the blast or the reverberatory types, one form of the latter (the "open-hearth" furnace) being specially used for steel. The highly corrosive effect of the slags formed during the smelting makes a basic lining desirable whenever possible, though grog bricks, and especially bauxite bricks, are used with fair success. Dense bricks of close texture, laid with thin joints, are required.

In lead and silver smelting, magnesia bricks make the most economical lining for smelting and cupelling furnaces. In the metallurgy of antimony, they are used in both shaft and reverberatory furnaces, and in tin and arsenic furnaces they are equally satisfactory. The linings of open-hearth furnaces for copper and steel are increasingly made of magnesia bricks; formerly, fireclay and bauxite bricks were chiefly used.

Steel furnaces are of several kinds, each of which has a special purpose. The most important are:

Converters, in which molten iron is converted into steel by blowing air through it (see p. 768).

Crucible furnaces, in which the steel is made in crucibles (see p. 770).

Electric furnaces, in which the materials are melted electrically (see p. 772).

Cupola furnaces (see p. 770).

Open-hearth furnaces (see below).

Rolling mill furnaces, in which the steel is reheated; in these, the temperature is not excessive, so that fireclay bricks and semi-silica bricks are quite satisfactory.

In many cases, only the most refractory bricks can be used, owing to the intense heat and the sudden changes in temperature to which they are subjected. So severe are the conditions in some steel furnaces that several kinds of bricks must be used in each, those bricks being chosen which have a special resistance to the dominating action of the contents at a particular portion of the furnace. Thus, in *malleable steel furnaces* the side walls are rapidly corroded by the slag undercutting them. To keep this corrosion at a minimum, the bricks used for the lower part of the side walls of the furnace up to the slag-line should be of fireclay mixed with fine grog, so as to produce a close texture. The bricks should be burned at 1600° C. or above, so as not to be affected by the temperature of the molten steel. Above the slag-line, the bricks should be equally hard-burned, but rather more porous, so as to withstand the variations in temperature. In the bungs, coarser bricks, burned at 1300° C., are preferable, as they are less sensitive to sudden changes in temperature.

Open-hearth furnaces are of two types, viz. those having an acid hearth and those having a basic hearth. The difference between them is in the nature of the refractory materials employed for the bottom or hearth, the acid hearth being lined with acid (siliceous) materials, whilst the basic hearths have linings of basic materials (magnesia, dolomite, etc.). Acid hearths have the advantage of providing for the rapid formation of silico-manganese (MnSi), which is one of the most powerful deoxidants, and thus produce better steels than basic furnaces; but the latter are extremely useful in the production of steel of fair quality from raw materials which contain too much phosphorus and sulphur for treatment by the acid process.

Open-hearth furnaces are constructed in a variety of ways, but usually the *roof* is built of silica bricks, as these have little or no tendency to shrink and so cause the collapse of the roof, as might be the case with fireclay bricks. Owing to the violence of the reactions which occur in the furnace, the silica bricks are corroded in the roof of open-hearth furnaces at the rate of 1½ to 2 inches per week, due to the action of fine dust. The slag, which at one part of the process of manufacture is frequently spurted on to the roof, also increases the corrosion, though to a smaller extent.

The *regenerators* are usually built of silica or fireclay bricks, but the checkerwork is preferably constructed of fireclay bricks, as the latter are less sensitive to sudden changes in temperature (p. 785).

The *sides* of open-hearth furnaces are usually built of silica or grog bricks, but in the basic furnaces the lower part of the sides is usually of dolomite or magnesia, which is surmounted by one or more courses of neutral (chromite) bricks; the upper parts of the sides are of silica, grog, or fireclay bricks. The use of chromite bricks in furnace linings as an intermediary between acid and basic bricks is not very good, as it softens and squeezes out. It is far better to build the walls of the furnace to a greater height than usual with magnesia so as to be well above the molten metal, in which case the acid and basic bricks may come into contact without doing any serious harm.

Chrome-magnesia bricks are superior to silica bricks in the roofs and side-walls of basic open-hearth furnaces, but they are liable to swell and "burst" as the result of the absorption of iron oxide from ferruginous slags.

The *hearth* of an *acid* open-hearth furnace is constructed throughout of silica or fireclay bricks, but it may be covered with a layer of silica sand, which is sintered by heating the empty furnace and then " washed " by the application of fused slag, which fills any crevices. The sand must be free from clay, which would cause spalling.

The hearth of a *basic* furnace is usually composed of a mixture of magnesia or dolomite and tar, but it is better built of magnesia bricks, to which a tamped lining of dolomite or magnesia and tar, 14 to 18 inches thick, may be applied. Lime bricks made of lime with 3 per cent. water-glass were used with much success in the earlier basic-hearth furnaces, but are seldom employed at the present time.

Magnesia bricks for use below the slag-line must resist slag and metal penetration, and should have a dense structure, with less than 20 per cent. porosity. Magnesia bricks exposed to the furnace atmosphere must resist spalling.

When magnesia bricks are used for constructing the hearth, three-quarters of the particles of sintered magnesia used for this purpose should be between $\frac{1}{12}$ inch and $\frac{1}{4}$ inch diameter; the remaining quarter should be in the form of magnesia dust. This material must be made plastic by the addition of one-eighth of its weight of hot tar. The use of finely powdered magnesia as a bond for tamping does not give satisfactory results.

Instead of a mixture of tar and magnesia, one consisting of finely ground sintered magnesia with 5 per cent. of ground basic slag from the furnace may be employed. This mixture sinters to a solid mass, which is somewhat stronger and more impervious than the one in which tar is used. The mixture must be applied in layers of not more than 2 inches thick, each layer being heated to vitrification before the next is added. About five layers are usually sufficient. This method of construction may appear expensive, but in practice it is cheaper and quicker to produce than a tamped hearth.

In some cases, the bottoms are made of magnesia bricks laid on edge and overlaid with a tamped dolomite-tar mixture in five 3-inch layers, each layer being fritted as soon as it has been applied. The use of dolomite has the disadvantage of " boiling " with the metal during the melting process, and this action appears to corrode the foundation bricks; it is, therefore, preferable to employ magnesia in place of dolomite whenever possible.

Magnesia bricks are unduly sensitive to changes in temperature, but recent tests of bauxite bricks show that if the latter contain less than 12 per cent. of silica, they are sometimes suitable for basic hearths. The author's investigations have shown that failure with magnesia bricks in basic steel furnaces have almost invariably been due to the use of (i) insufficiently burned magnesia, (ii) magnesia of too impure a quality, or (iii) defective workmanship; the first and second causes being by far the most important. Properly made magnesia bricks do not shrink on heating, nor are they specially sensitive to sudden changes in temperature; bricks of this material which have not been sufficiently well burned are, on the contrary, highly sensitive to temperature changes and spall readily.

Although a basic material has been found advantageous for the bed or bottom of many furnaces used in steel-making, as already explained, it would not be suitable for the roof arches, because of their contraction on being heated. Hence, until unshrinkable basic ones can be produced, it is necessary to build the roof with acid bricks. The acid and basic bricks are generally separated by a course of neutral material, such as chrome iron ore.

Magnesia bricks are almost ideal, if properly made, for use in open-hearth furnaces, but they are very costly and cannot, for that reason, be used so largely as might be desired. Where they are employed, their destruction is caused almost wholly by cracks due to shrinkage; very little corrosion by slags or gases occurs. Occasionally, however, the alkaline oxides in the furnace lining are reduced at about 1500° C., yielding metals which are powerful catalytic agents, and may bring about unsuspected reactions—including the conversion of magnesia into an agent which oxidises steel and possibly nitrogenises it. Hence, the proportion of these oxides in the refractory materials should be very limited.

The use of chrome-magnesia bricks, instead of plain magnesia bricks, offers several advantages.

The cost of magnesia bricks or chrome-magnesite bricks should not be allowed to influence their use unduly, because furnaces lined with these bricks can be worked at much higher temperatures, and therefore have a much larger output, than those in which other bricks are used for the lining.

In the *ports and uptakes*, where the velocity of the waste gases is great, owing to the constriction of the passages, corrosion is somewhat irregular, but is specially pronounced at sharp turns where the gases impinge on the surfaces. These surfaces, which are bombarded by the larger-sized particles of iron oxide, are subject to heavy fluxing, the fused material flowing in a thin sheet into the slag pocket.

The ports and uptakes of open-hearth furnaces should be made of specially resistant bricks, as the cutting action of the flame is very intense and furrows soon appear even with bricks of the best quality. The abrasive action of the fine dust from the producer gas shows its mark along the sides of the furnace.

Silica bricks withstand the severe conditions to which the greater part of the brickwork is exposed as well as any bricks yet tried, and, except for the hearth of a basic furnace, they have the further advantage that their fusibility is not appreciably modified by their absorption of a high proportion of iron oxide. As some of the bricks in open-hearth furnaces are required to resist a temperature up to 1700° C., they should not contain more than 5 per cent. of impurity, including the 1½ to 2 per cent. of lime used in bonding the bricks.

It is, of course, impossible to control the whole of the conditions necessary for the satisfactory maintenance of open-hearth furnaces by a proper selection of the bricks, as, unless proper care is taken in controlling the furnace, it is obvious that the strains put on the bricks must, sooner or later, cause their collapse. The falling of bricks from the roof and sides of a furnace are frequently caused by the sudden expansion or contraction of the walls due to bad controlling of the gases. This naturally facilitates the action of the molten slag and gases, causing the premature disruption of the wall, even when no fault can be found with the bricks.

The chief causes of disintegration in open-hearth furnaces are the corrosive action of mixtures of basic flue-dust and volatilised oxides, abrasion, sudden changes of temperature, and molten slag. It is, therefore, necessary that the refractory materials used should be as resistant as possible to these sources of damage.

Several attempts have been made to find better materials, and G. G. M'Murtry has patented the use of zirconia in linings for acid or basic open-hearth furnaces, but the price of the mineral has been too high to try out the idea on a commercial scale. It has been found, however, that zirconia bricks have outlasted silica bricks when placed side by side in a very hot part of an open-hearth furnace.

The marked increase in the life of the open-hearth roof in recent years is noteworthy. A few years ago an average of 250 to 275 heats was considered fairly good. To-day an average of 400 to 500 heats is not uncommon, and single runs up to 800 to 900 heats are frequent. While by far the largest share of the credit for this marked change is unquestionably due to improved furnace-design, methods of operation and better bricklaying, some credit is due to the better bricks now being used.

The use of *insulating bricks*, in order to retain some of the heat otherwise lost in open-hearth furnaces, is increasing. The proportion of fuel saved by this means is attractive, and it is probable that insulating bricks will be used in all new furnaces.

Stoves are used for so many purposes that it is almost impossible to describe the kind of firebricks used in them.

Heating stoves used in houses and factories are usually lined with fireclay bricks; No. 2 grade bricks are quite suitable and bricks of inferior quality are often used.

Air stoves, used for heating the air for blast furnaces, etc., are described on p. 753.

Surface Combustion Furnaces.—The important discovery made independently by Bone and Schnabel, that an explosive mixture of gas and air passed through a porous diaphragm made of refractory material and ignited at the surface of the latter has special advantages when applied to technical heating devices, has created widespread interest both in the selection of suitable refractory materials and in the practical application of this form of "surface combustion."

According to W. A. Bone, only those refractory materials are satisfactory which act as catalysts, but this does not cause serious inconvenience, as all incandescent surfaces accelerate gaseous combustion, and at incandescent temperatures all become approximately equal catalysts. Knietsch also found that above 850° C., porcelain, platinum, and ferric oxide are all equally good catalysts in converting sulphur dioxide into sulphur trioxide. Bone also found that (i) combustion occurs only in layers immediately in contact with the incandescent surface; (ii) the catalysis depends on the absorption of the gases by the surface, thereby producing the effect of high concentration or high pressure; (iii) the incandescent surface becomes strongly negatively electrified during the combustion; (iv) the mixed gas and air must be passed through the porous body at a velocity greater than the speed of ignition; (v) after the attainment of a steady condition, the rate of combustion depends on the pressure if the gases are in their combining proportions and the products of combustion are quickly removed. When one gas is in excess, the rate of combustion is proportional to the partial pressure of the combustible gas.

The refractory material originally used was fireclay, to which sufficient fine sawdust or other organic matter has been added to give the burned material the necessary porosity. Many of the difficulties experienced in the use of this discovery have been due to the fireclay diaphragm not being sufficiently refractory. It is not unusual for a temperature approaching 2000° C. to be reached in parts of the diaphragm, and the fusion which then occurs when fireclay is used soon renders the diaphragm useless. This difficulty is largely avoided by the substitution of corundum for the greater part of the fireclay, only sufficient clay being used to give the necessary binding power, or by using a mixture of graphite and tar, which when baked has the required porosity.

Other oxides which may be used include alumina, magnesia, beryllia, chromite, and zirconia. The "activation by acid" of these oxides is claimed in Eng. Pat. 426,325—1933. A method for making diaphragms in two layers, each composed of grains of different sizes, was patented in 1924 (Eng. Pat. 245,182).

Instead of a diaphragm with fine pores, the gaseous mixture may be passed through a vessel packed with broken firebrick or other refractory material; this modification is specially useful for heating crucibles, multitubular boilers, muffles, retorts, and appliances where internal heating is required.

Flameless surface combustion [1] has also been used successfully for smiths' hearths, tempering furnaces, heat-treatment furnaces for artillery, heating type metal, and generally where radiant heat is required. By means of flameless combustion much higher temperatures are attainable with a given gas than by the ordinary methods of flame combustion without a regenerative system, as with any gas of high calorific intensity (such as coal-gas, water-gas, or natural gas), the upper practicable temperature limit is determined by the refractoriness of the material composing the chamber to be heated rather than by the possibilities of the actual combustion itself.

Tar stills require firebricks of good quality for the interior of the furnaces, but Staffordshire blue bricks are preferable for exterior work.

Tin-smelting furnaces require to have linings and hearths selected and laid with special skill, if they are to have a long "life," because tin escapes so readily in several different forms. For the greater part of the structure, well-shaped, hard-burned fireclay (grog) bricks are quite satisfactory; they need not be highly aluminous, as the latter type increase the difficulties of recovering the tin from old hearths. Where much antimony is present in the tin-ore, the hearth should be covered with chromite and the walls should be lined with magnesia bricks, so as to prevent the formation of antimony aluminate, which rapidly disintegrates bricks, or a lining of magnesia may be used. The amount of corrosion is usually small, so that the chief requirements are that the bricks shall be sufficiently refractory and not unduly absorbent of the metal.

White-metal furnaces are used for preparing white metal and similar alloys (including anti-friction bearing metals, solders, pewters, type-metal, and other mixtures of tin, lead, antimony, and copper), and for the recovery of these metals from "ashes" and "white-metal residues," all of which yield products having a strong penetrating action. Reverberatory furnaces are chiefly used for recovery work, but rotary furnaces are largely employed for melting the mixtures used to form white metals.

The hearth of the reverberatory furnace is usually of fireclay bricks covered with chromite or of chromite over magnesite. In some cases, the hearth is built inside a cast-iron tank, so as to prevent loss of metal by leakage, and a cast-iron core is used inside the bridge for the same purpose. The loss of metal is seldom due to actual corrosion, but to the metal passing through cracks or defective joints. If, therefore, these can be avoided, there will be little or no leakage. For this reason, a sintered hearth is sometimes formed on the hearth proper, glass cullet being used to form it. Chromite hearths have no special advantage, nor have those of magnesite, as a highly refractory hearth is not required, but an impervious one. Some firms prefer a hearth made of fireclay brick, on which a 12-inch layer of broken glass has been fused, to any other type of hearth.

Zinc-smelting Furnaces.—The refractory materials required in furnaces employed in smelting zinc are of four classes: those in furnaces used for *roasting* the ores need not be highly refractory, but must be thoroughly well

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[1] The patents covering the commercial application are under the control of the Spencer Bonecourt Co., Ltd.

burned, or they will shrink when in use; the bricks must not be sensitive to sudden changes in temperature, so that fireclay bricks are chiefly used.

Bricks in furnaces used for the *distillation* of zinc must withstand very trying conditions. The temperature of the furnace is usually about 1250° C. to 1350° C., and at this temperature the retorts are required to withstand the corrosive action of the zinc vapour and must, therefore, be sufficiently free from impurities to avoid contaminating the zinc vapours with zinc sulphide or other injurious substances. The other important requirements are: mechanical strength, tenacity, resistance to sudden changes of temperature, low permeability, and durability. Great refractoriness is less important than mechanical strength and resistance to corrosion.

When zinc oxide is heated with silica, the orthosilicate ($2ZnO.SiO_2$) is formed at about 1000° C., but in the presence of clay a mixture of zinc orthosilicate and zinc aluminate (spinel) is formed. Both these substances are readily fusible and form slags which corrode, and eventually destroy, the retort.

The principal cause of disintegration in zinc retorts is the corrosive action of the gases and slags formed during the distillation of the metal. Consequently, a lean clay or, preferably, a mixture of clay and grog should be used. Iron compounds may be reduced to ferrous oxide or to metallic iron, which may then form a slag with a highly corrosive action on the retorts. Manganese and lead silicates also corrode the retorts, but calcium and magnesium silicates alone are not very harmful, though in combination with ferrous and manganese silicates they are highly corrosive. For this reason, the custom of adding lime to the charge has been discontinued.

Where the heating of the retort is carefully controlled, the zinc slag should be practically neutral, so that it may remain in contact with the retort for a considerable time without damaging the latter.

In use, the walls of a zinc furnace are gradually vitrified, during which time they become less refractory and the changes of temperature are much more liable to cause cracks in the retort. The strength is, however, increased.

A highly aluminous material, low in silica, is generally suitable for zinc retorts. The alumina in the clay is gradually converted into a zinc aluminate spinel containing about 1 per cent. of ferrous oxide, with a specific gravity of 4·45 to 4·52, which is not attacked by any acid except boiling sulphuric acid.

In Belgium and Spain, the retorts are highly siliceous, thinner, and of a greater thermal conductivity, but they are less resistant to the corrosive action of the charge. In Belgium and Westphalia, the retorts are sometimes glazed externally to render them impervious to zinc vapour.

The use of magnesia for retorts and muffles has been suggested by Steger, on account of its greater thermal conductivity, basic character, giving greater resistance to corrosion, higher refractoriness, and impermeability to zinc vapour. The application of protective coatings of zirconia or fused alumina, and the admixture of carborundum with the retorts, are worth further attention.

Zinc retorts only last a very short time—usually thirty to forty days—on account of the rapidity with which they are vitrified and corroded.

The bricks used for lining *electrothermic distillation furnaces* for zinc require to possess properties similar to those of retorts. Fireclay (grog) bricks are chiefly used, but the possibilities of mullite bricks, fused alumina, and fused sillimanite bricks are worth investigation. Silica and zirconia bricks are too readily attacked.

The linings of *spelter furnaces* must be close-grained, strong, and sound, so as to withstand changes in temperature between 800° C. and 1400° C., as well as the action of gas, slag, etc.

Monolithic Linings for Furnaces.

For many years, certain portions of furnaces—such as the hearths—have been made of monolithic material, such as ganister, white sand, crushed silica rock, dolomite, magnesite, etc. More recently refractory cements (p. 723) and refractory concrete (p. 746) have been used for these and other purposes in furnace construction. The chief reason for using a monolithic structure is to avoid the weakness due to joints in brickwork.

To consolidate such materials, it is usually necessary to tamp or ram them by repeated blows from a suitable tool, the product being known as a *tamped hearth* or a *tamped lining*. If a *plastic paste* is used it should be "stiff," *i.e.* of the consistency of damp soil, as softer pastes do not consolidate well on tamping. If a *dry material* is used it is mixed to a paste with water,[1] and is applied to the interior in one of several ways. The usual method is to put inside the converter a core of plates or pieces of wood in a suitable position, so that with the brickwork of the furnace a temporary mould is formed. The lining material—which is usually ganister or a mixture of dead-burned magnesia and tar [2]—is poured into this " mould," and is tamped into position with a wooden beater shod with steel. If a tar bond is used in the mixture, the furnace should be kept warm during the ramming—in any case it must be heated very gently at first in order to dry the lining thoroughly before commencing to " burn " it.

In another method, the crushed material (often termed the "sand") is placed on the furnace-bottom in layers, the lower ones consisting of sand and silica rock, whilst the upper layers contain more and more pure sand. Thin layers are put on and " burned in " before applying further layers. This process is continued until a thickness of about 3 feet is reached. During the " burning in," some of the quartz is converted into tridymite, and so the hearth is bound closely together by the interlocking crystals. In order to accelerate the action, iron oxide or slag is often added to act as a catalytic agent.

Other tamping mixtures may be placed in position in moderately thin layers, each layer in turn being well consolidated by tamping.

For patching work, the surface to be repaired should be chipped free from slag and then wetted with a wash of water and clay of about the consistency of decorator's distemper, as the ganister adheres well to this. A ball of ganister is pressed against the damp surface, worked out with the hands and beaten with a suitable tool, more mix being added if required. Instead of ganister, any other suitable material may, of course, be used. The consistency of the mixture and the proportion of water present are of great importance. Too wet a mixture cannot be properly consolidated, and some mixtures, which are deficient in water, never gain the requisite strength, but remain friable and crumbly. The face of the monolithic work should be left smooth, and after a few hours a gentle heat can be applied.

With most refractory cements and refractory concrete, it is best to allow 24 hours, and when concrete is used the work should be kept wet through-

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[1] Many masons do not mix the ganister mechanically, but wet it and allow it to stand for two or three days if dry, and a less time if moist. The ganister for furnaces should have the consistency of soft putty; over-watering is not necessary and only enough to soak it through should be used, but there should be no dry places in the pile. Just before use, the ganister should be turned repeatedly and mixed until it is tough enough to knead into balls; when this stage is reached it is fit for either lining or patching purposes.

[2] Thomas & Gilchrist's (1880) patent for a basic lining specifies the use of two to four volumes of hard-shrunk magnesian limestone (made by calcining the stone at a white heat) and one volume of tar, mixed in a steam-jacketed pug mill (see *Dolomite*, p. 801).

out the whole of this period, in order to develop the hydraulic power of the cement. Material which is applied in an almost dry state and mechanically tamped or rammed can be dried almost immediately, but refractory concrete should not be treated in this manner.

The initial heat should be very gentle, so as to evaporate the water slowly; if it is driven off too rapidly it will produce cracks. A further period of gentle heating is necessary at 500° C. to 600° C. if the material contains sand or other form of raw silica (quartz).

When skilfully made of suitable materials, tamped and other monolithic linings are very durable. In some instances, they have been in constant use for seven years or more.

Ganister or other form of crushed silica rock is generally used for acid linings, but sometimes a *white sand* is used. In either case, the material should not contain less than 95 per cent. of silica, and 98 per cent. or more is preferable. The iron oxide should not exceed 0·5 per cent., and the sum of the lime and magnesia should not exceed 2 per cent.

The grains should be as angular as practicable and should be between 30- and 100-mesh. Fine dust should be avoided as it tends to entrap air, which prevents consolidation, but 10 per cent. of material less than 100-mesh need not cause any trouble.

Perfectly pure silica lacks cohesion when heated, so that a small proportion (not exceeding 10 per cent.) of clay in the material is an advantage. The addition of a very small percentage of felspar also assists the cohesion of the particles when heated. Hence, if the material contains a little clay or other substance which causes it to become plastic when wetted and milled, this is an advantage.

It is difficult to obtain a perfectly homogeneous mixture by adding fireclay to crushed silica rock, but fairly satisfactory results can be obtained by prolonged treatment in a wet pan mill. The addition of lime to ganister to make it plastic is objectionable, as the lime reduces the refractoriness.

According to H. T. Chappell (U.S. Pat. 1,308,481), furnace linings containing silica may be improved and rendered more resistant by heating to a temperature at which they are softened and then applying to them finely ground calcined alunite.

Dolomite is used for lining converters employed in the Thomas and Gilchrist or basic process; it should previously have been sintered, crushed to a granular powder, and then mixed with tar. The proportions actually used vary within wide limits, but excellent results can be obtained by placing 3 cwt. of sintered dolomite in pieces ⅛ to ¾ inch diameter, 1 cwt. of similar dolomite ground to a fine powder, and 80 to 90 lbs. of hot tar in an edge-runner mill with a revolving pan and mixing thoroughly. The warm mixture is rammed into place round a core by means of a hot-iron rammer. Alternatively, iron moulds may be filled in a similar manner to that used for carbon bricks. For the hearth of basic, open-hearth furnaces, the magnesian lime is spread in thin layers, each of which is fritted by the heat of a fire before another is put on.

According to Meyer,[1] the product of a shaft furnace is preferred to that of a rotary furnace. Some furnace managers mix the dolomite with ground basic slag for use in burning in new hearths or for very heavy repairs.

In preparing dolomite linings, it is not necessary to use only newly calcined dolomite. Material obtained from old linings may be crushed, screened so as to separate the excess of tar and dust, and then used instead of the coarser

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[1] *Stahl u. Eisen*, 1936, **56**, 875.

dolomite previously mentioned. In this case, only about half the amount of tar mentioned will be required. (See *Basic steel furnaces*, p. 795).

Magnesia is used similarly to dolomite, but is more difficult to repair.[1]

Although the price of dead-burned magnesite is greater than that of dead-burned dolomite, it has been found that in most cases where magnesite is used the total cost over long periods is considerably less than with dolomite. This is largely due to a magnesite hearth being more durable and requiring less repairs than one of dolomite.

Some furnace masters do not use dead-burned magnesite, but only magnesite bricks which they grind to powder of suitable grade. The bricks are regarded as being superior to the dead-burned magnesite of which they are made.

Bull-dog.—This is a mixture of ferric oxide and silica made by roasting tap cinder with free access to air. Tap cinder is a basic silicate of iron—$2FeO.SiO_2$ or thereabouts—and, on roasting, it takes up oxygen and gives a mixture of ferric oxide and silica. As these do not unite, the substance is infusible in an oxidising atmosphere, but under a reducing one the clinker is re-formed. Bull-dog is applied in the same manner as sand.

Carborundum.—A mixture of 75 per cent. of carborundum and 25 per cent. of sodium silicate has been used in Germany for converting common bricks into refractory bricks. The mixture is applied to the thoroughly dried bricks and the coating is dried twenty-four hours before being slowly heated and burned in. The firmly adherent glassy veneer of carborundum produced may be not more than $\frac{1}{50}$th of an inch thick, yet it has a remarkable resistance to mechanical injury, endures very high temperatures, and gives protection against the chemical action of flames. Sudden changes of temperature appear to have little effect on it. The coating is stated to have been successfully used in gas retorts as well as on the outside, and a paste of 50 per cent. of carborundum and 50 per cent. of clay serves for repairs when cracks appear.

Refractory cements (p. 723) and *plastic refractories* (p. 746), including *refractory concrete* (p. 746), are also used for monolithic or tamped linings, though the consistency must, usually, be stiffer when the material is to be consolidated by tamping. It should then have the same consistency as moist earth.

The grading of the material to be used for tamping is important; it should contain particles of many sizes so that they interlock well, but too many grades are inconvenient; three are usually satisfactory.

Chesters and Lee[2] have found that the best coarse-tamped linings, containing up to 50 per cent. of ½-inch to ¼-inch material and having porosities as low as 20 per cent., can best be made by control of the grading, using three grades:

Grade.	Size.
(*a*) ½-inch to ¼-inch material,	0·5 inch to 0·25 inch.
(*b*) 7- to 25-mesh,	0·095 inch to 0·024 inch.
(*c*) through 25-mesh,	less than 0·024 inch.

The densest mixture consists of

46–50	per cent.	of grade	(*a*)
18–20	,,	,,	(*b*)
36–30	,,	,,	(*c*)

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[1] Dolomite is frequently employed to repair magnesia linings, as it is much easier to use.

[2] *Trans. Cer. Soc.*, 1937, **36**, 9.

This mixture tends to segregate and is improved by reducing grade (*a*) to 10 per cent., and increasing grade (*b*) to 30 per cent. and grade (*c*) to 60 per cent.

REFRACTORY MOULDS.

The moulds used in casting iron, steel, and other metals and alloys are made of various refractory materials, of which sands or mixtures of sands and clay are the most important, though plumbago and numerous other materials are used to produce a suitable " face " or " finish."

The various moulding sands and their uses are described in the author's *Sands and Crushed Rocks* (Frowde and Hodder & Stoughton).

The " compo " which is used in casting steel is of very variable composition, each foundry having its own special mixtures. It consists chiefly of burned fireclay (grog) or ganister and raw clay, with some coke-dust.

CHAPTER XIX.

TESTING REFRACTORY ARTICLES.

THE testing of refractory articles is beset by numerous difficulties on account of the nature of the materials. Much information may be gained by a careful inspection of the article and noting the accuracy, or otherwise, of its various dimensions, its *shape, colour, texture, density, hardness, resistance to hammer-blows, " ring " when struck,* etc.

A *chemical analysis* is chiefly of use in comparing articles from various sources or in tracing the origin of some defect, such as unusual fusibility or distortion. In itself, a chemical analysis is of minor value, as the usefulness of a refractory article depends far more on its physical properties than on its chemical composition.

A *micro-petrological examination* is often of great value, particularly in the case of mullite, silica, and magnesia bricks. It should include ascertaining the proportion of each mineral present, the arrangement of the particles in relation to each other and general observations on the soundness of the structure.

A micro-petrological examination usually requires:

(i) A microscopic examination of thin sections; (ii) a determination of the specific gravity and a calculation of the various mixtures which will have the same specific gravity; (iii) staining with suitable dyes, which have a distinctive effect on some minerals; (iv) producing a time-temperature graph showing the changes which occur during heating and cooling; (v) optical methods, such as the determination of the refractive index, which differs with each modification of each oxide; and (vi) determining the expansion-temperature curve, which enables the presence and, to some extent, the respective proportions of the various minerals to be ascertained.

The *refractoriness* or fusibility of the article is one of the simplest properties which can be used for recognising the value of a refractory material, though its importance must not be exaggerated. The test must be carried out under uniform conditions (p. 809) or the results will not be comparable. Thus, by heating the material very rapidly an unduly high result will be obtained.

The test-piece should consist of a tetrahedron of the same shape as a Seger cone, but having the sides of the triangular base ½ inch in length and the height 2 inches. The test-piece is cemented on to a refractory plate (with a mixture of highly calcined alumina and 10 per cent. of china clay) and is surrounded by Seger cones. The cone which bends so that the apex touches the base at the same time as the test-piece is regarded as of equal refractoriness. This test is often known as the *squatting test.*

A modification in which the first signs of fusion of the test-piece are compared with the bending of Seger cones is sometimes known as the *refractoriness safety test* (see p. 809). This gives a lower result than the *squatting test.*

The *refractoriness-under-load* is probably the most useful single test of a refractory material. It is determined in various ways (see p. 362), but the most usual method is to heat a test-piece 3½ inches by 2 inches by 2 inches under a constant load of 50 lbs. per square inch at a temperature which rises steadily at the rate of 50° C. per five minutes, and to record the changes in height at every 10° C. rise in temperature until the test-piece collapses. The results should be recorded in the form of a graph.

The *rate of vitrification* as shown by a series of porosity tests on the material at various temperatures, the results being expressed in the form of a graph, is often very useful in indicating the behaviour of refractory materials when in use.

The *change in volume* (expansion or contraction) when the article (or a portion of it) is re-heated to a predetermined temperature will give some idea of the change likely to occur in the article when it is in use. In large structures, and particularly in arches, it is of great importance to use materials which are as constant in volume as possible over a large range of temperature (see p. 809).

It is not always sufficient to measure the size of the article before re-heating and again when it is cold; a much more important measurement in many cases is that of the article at the highest temperature it will attain when in use.

A valuable paper on the reversible thermal expansion of refractory materials and methods of measuring it has been published by Rigby and Green.[1]

Sensitiveness to sudden changes in temperature and *resistance to thermal shock* are usually estimated from the results of a *spalling test,* of which there are several forms, none of which is completely satisfactory. The most popular test consists in heating a panel of the bricks to a pre-arranged temperature (usually 850° C. in Germany, and 1000° C. in this country and America, but 1440° C. in the American Navy tests) and then cooling rapidly with a blast of air. The test is repeated until the bricks are too disintegrated to remain *in situ*, and the number of repetitions of the test is assumed to measure their resistance to thermal shock. Consistent results can be obtained with bricks of the same kind from one works, but the test is too crude to be really satisfactory.

The standard tests for resistance to spalling in the United States [2] require a frame in which the bricks form a panel not less than 18 inches square, with a 9-inch × 2½-inch surface of each brick exposed to the heat. The bricks are surrounded by other refractory bricks. All the bricks are to be laid in refractory kaolin, with joints not exceeding $\frac{1}{16}$ inch thick. Before insertion in the frame, each brick is numbered on the back and weighed. The panel is arranged to form part of the front or back wall of a special furnace, and is backed by suitable heat-insulating material so that the heat loss is approx. 900 B.T.U. per hour. In this furnace, the panel is heated to a specified temperature for at least 3 hours, so as to dry and warm it. Afterwards the panel is heated to the spalling temperature (1400° C.) and retained at that temperature for 10 minutes, and then cooled by an air-water blast for 10 minutes. The cooling is effected by an air-water mist delivered through an opening 24 inches × 3½ inches by means of four spray units, each delivering 2½ gallons of water during 8 minutes and air at 400 cubic feet per minute, for 10 minutes. The cooler is operated reciprocally, so that each brick is in contact with the spray 125 times in 10 minutes. After heating and cooling the requisite number of times, the

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[1] *Trans. Cer. Soc.*, 1938, **37**, 355.

[2] *American Society for Testing Materials*, Standard Methods C38–36, C107–36, and C122–37.

bricks are re-weighed, and the loss is recorded as a percentage of the original weight. In the second and subsequent re-heatings, the bricks are placed in a different order in the panel. Twelve heatings and coolings with water and two more without it are specified. Adherent pieces of bricks must not be detached. The kaolin is removed with a trowel.

Spalling tests on single bricks give uncertain results. Norton[1] gives the following figures (number of times heated and cooled) as showing comparative resistance to spalling:—

Silicon carbide	21–29	Zircon bricks	3
Fireclay bricks	4–42 (mean 14)	Fused alumina bricks	2
Kaolin ,,	20	Chrome ,,	2
Mullite ,,	16	Spinel ,,	1
Bauxite ,,	15	Magnesite ,,	1
Zirconia ,,	6	Silica ,,	1

Some of these figures do not agree with those of other investigators.

The *crushing strength* of firebricks is always so much greater than is necessary that there is little to be gained by determining it. A knowledge of the crushing strength of retorts, crucibles, etc., is more important, but the test must be made on the whole article and not on a part, and it should show, as far as possible, the behaviour of the article when in use. For instance, a horizontal retort or a crucible is seldom, if ever, subjected to any pressure from above, but its capacity for resisting the pressure of its contents is important.

The crushing strength at the highest temperature attained in actual use is often more important than that of the cold article.

The *porosity* of various refractory articles is sometimes important, and gives valuable clues to undesirable properties, causes of defects, etc. The size and distribution of the pores are often more important than the total percentage of porosity.

The *apparent porosity* indicates the percentage volume of air spaces (unsealed pores), and may be determined in two ways:

(*a*) A cubical test-piece of about 2 inches side is dried at 110° C. and cooled and weighed. It is then soaked in water (preferably boiling for 2 hours); after cooling overnight the test-piece is wiped dry and again weighed. The increase in weight is that of the water absorbed in the pores.

(*b*) A more accurate method consists in immersing the dried and weighed test-piece in paraffin overnight,[2] preferably under reduced pressure, and then weighing the test-piece whilst it is suspended in paraffin. The test-piece is then wiped dry and again weighed.

If W_a is the weight of the dry test-piece,
W_b ,, ,, ,, test-piece when soaked with paraffin,
W_c ,, ,, ,, test-piece suspended in paraffin;

the *apparent porosity* is

$$\frac{W_b - W_a}{W_b - W_c} \times 100 \text{ (per cent. by volume).}$$

The *true porosity*, which includes both sealed and open pores, is

$$\left(1 - \frac{S_a}{S_t}\right) \times 100,$$

where S_a is the apparent specific gravity or bulk density,
S_t is the specific gravity of the powdered material.

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[1] "Refractories for Industrial Furnaces," *Fuels and Furnaces*, 1932, **10**.

[2] A much longer soaking is sometimes needed by very dense materials.

The *bulk density* or *apparent specific gravity* (S_a) of the material is found by using the following formula, in which G is the specific gravity of the paraffin (see *below*):—

$$S_a=\frac{W_a}{W_b-W_c}\times G.$$

The *true specific gravity* is determined on the powdered material, the particles of which must be so small that they contain no sealed pores. If the material passes completely through a No. 120 British Standard Specification sieve it will usually be sufficiently fine. It should be dried at 110° C. before being tested.

A specific gravity bottle of about 50 c.c. capacity is dried and weighed. About 10 to 15 grams of the dried powder is introduced and the bottle and contents weighed. The bottle is then nearly filled with paraffin, placed in a vacuum desiccator and allowed to stand *in vacuo* for four hours or more. The bottle is then filled with paraffin, the stopper inserted and any surplus paraffin wiped off. The bottle and contents are then kept at a suitable temperature (usually 25° C.) for at least an hour, after which they are again weighed.

Weight of empty bottle and stopper . . . . $=a$ grams.
Weight of empty bottle and stopper and powder . . $=b$ „
Weight of empty bottle and stopper and powder and paraffin $=c$ „
Weight of bottle and stopper filled with paraffin . . $=d$ „
Weight of bottle and stopper filled with water . . $=e$ „

True specific gravity of powder $=\frac{b-a}{(d-a)-(c-b)}\cdot\frac{d-a}{e-a}.$

The same precautions are to be taken when the bottle is filled with paraffin and also when it is filled with water. The expression $\frac{d-a}{e-a}$ is the specific gravity of the paraffin.

The *unaltered quartz* in a silica brick can be approximately estimated from the true specific gravity of the material. Quartz may be assumed to have a specific gravity of 2·655 and both cristobalite and tridymite a specific gravity of 2·322. If S is the specific gravity of the powdered brick, the percentage by volume of unaltered quartz is

$$\frac{796\cdot5}{S}(S-2\cdot322).$$

When possible, this result should be checked by a micro-petrological examination, and by the following modification of Rosival's method, proposed by A. Scott,[1] which gives in about an hour the percentage of unaltered quartz, with an error of less than 1 per cent. When a very thin section of the brick is viewed through a microscope, between crossed nicols, using a ¼-inch objective, the quartz is readily distinguished by its yellow interference colour and by its clear surface. A series of 6 or 8 lines is then drawn on the slide parallel to one edge of the slide, and a second series at right angles to the first. The slide is then adjusted so that one of the lines coincides with the cross-wire of the eye-piece, and the whole of the section along that line is made to traverse the field of view by means of a mechanical stage. The intercept of each quartz crystal is measured by means of a micrometer eye-piece. Any " hole " is measured and deducted. The intercepts on all the other lines are similarly

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[1] *Trans. Cer. Soc.*, 1918, **17**, 188–191.

measured, added together and divided by the sum of the intercepts made by the section along the two sets of lines. It is desirable to measure intercepts totalling about 1500 units.

The *permeability* may be useful in some cases, though usually it is not necessary.

The *resistance to corrosion* by fluxes can only be tested empirically at present, and the results of such tests should be applied with caution.

The *resistance of the material to abrasion* is of value for materials used in furnaces, and is usually determined by holding a brick at a constant pressure in contact with an abrasive wheel travelling at a standard speed.[1]

The *resistance to weather and frost* may be important for refractory materials in exposed situations, though, in most cases, this is unnecessary.

The *conductivity* of heat and electricity can be determined with fair accuracy at any desired temperature. It is important that the temperature selected should be one at which the bricks are used, or the test will be of little value. The determination of thermal conductivity is important in connection with efforts to reduce the loss of heat in kilns and furnaces.

The following thermal conductivity factors are useful:—

To convert B.T.U./(hr.) (sq. ft.) (° F./ft.) multiply by:

12	to obtain	B.T.U./(hr.) (sq. ft.) (° F./in.);
12	,, ,,	pound-cal./(hr.) (sq. ft.) (° C./in.);
0·00413	,, ,,	g.-cal./(sec.) (sq. cm.) (° C./cm.);
173	,, ,,	kilo-ergs/(sec.) (sq. cm.) (° C./cm.);
0·0173	,, ,,	watts/(sq. cm.) (° C./cm.);
1·49	,, ,,	kg.-cal./(hr.) (sq. m.) (° C./m.).

X-ray analysis is invaluable for identifying certain minerals in refractory materials, and in some cases (*e.g.* chrome ore) it enables their source to be stated.

Temperature-property graphs, showing the changes of various properties with an increase in temperature, are often valuable. The most important graphs are those relating the changes in temperature to changes in compressive strength, tensile strength, torsional strength, expansion, thermal conductivity, and electrical conductivity.

The *durability* of any kind of firebrick, retort, or crucible cannot be ascertained reliably by any tests at present in use, as so much depends on the circumstances in which the article is used.

Further information will be found in the various specifications summarised in the next chapter, and in the author's *British Clays and Sands*, in his *Clayworker's Handbook*, and in his *Chemistry and Physics of Clays and Other Ceramic Materials.*

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[1] No really satisfactory method of determining this has yet been devised, so that rather crude methods are necessarily employed.

CHAPTER XX.

SPECIFICATIONS.

THE following summarised specifications indicate the semi-official standards in use at the present time. They are all somewhat tentative, and are in no sense obligatory except by agreement.

SPECIFICATION FOR GAS RETORTS

(Institution of Gas Engineers, 1934).

Definition.—A moulded retort is defined as a complete section of a retort without longitudinal joints, manufactured from fireclay or siliceous material. A segmental retort is regarded as composed of bricks, blocks, or tiles, and these must conform to the Specification for such articles.

Refractoriness Safety Test.—Test-pieces of the material should show no " signs of fusion " when heated to Seger Cone 28 (about 1630° C.) in a suitable furnace at the rate of 50° C. per 5 minutes after about 1000° C. has been reached.

The test-pieces are tetrahedra with base-sides ¾ inch and a height of 1½ inches.

The " signs of fusion " are (i) the angular edges begin to lose their angularity, (ii) the test-piece bends, and (iii) the matrix runs out.[1]

Chemical Analysis.—A complete chemical analysis of the material is to be provided, when required by the purchaser, for his personal information only.

Surfaces and Texture.—All the surfaces shall be reasonably true, and, after burning, no washing shall be done without the consent of the purchaser. The material shall be evenly burned throughout and of regular texture.

After-contraction or -expansion.—Two test-pieces, each 2½ inches to 3 inches by 1½ inches to 2 inches with parallel ends, when heated up to 1410° C. in at least 4 hours, maintained at that temperature for 2 hours in an oxidising atmosphere and then allowed to cool, shall not show an average after-contraction or -expansion of more than 0·75 per cent., with a tolerance of 0·1 per cent. for experimental error.

Variation in Dimensions.—Moulded retorts shall be true to template in cross-section, straight longitudinally, of even bore throughout, uniform in thickness and not warped or twisted. The maximum permissible variation from the straight shall not exceed ¾ inch in 7 feet of length or ± ¼ inch in any direction of a cross-section.

Inspection and Testing.—Pieces of retorts, representative of the bulk, may be selected for testing, either before or after-delivery. Representatives of

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[1] This test gives lower results than that in which the top of the test-piece bends and almost touches the base.

the maker and user shall, if they choose, be present when such selection is made and shall be supplied with portions of the material taken for testing.

Any complaint as to quality of material shall be made by the purchaser before the expiration of ten days after delivery.

No consignment is to be rejected on the results obtained by a single sample, because of the possibility of "freaks."

If the engineer (or purchaser) and the maker are not prepared to accept each other's tests, they shall agree to submit the samples for testing to an independent authority to be mutually agreed upon, and the engineer (or purchaser) reserves to himself the right, if the material does not conform to the tests laid down in the specification, to reject any or all the material in the consignment from which the test-pieces were taken.

The cost of these independent tests and of any retort lengths or tiles damaged before delivery for obtaining test-pieces shall be divided between the purchaser and the maker if the test proves satisfactory, and if unsatisfactory such cost and that for all other subsequent tests required on this account from the same consignment shall be borne by the makers.

The cost of any tests or of any material damaged for the purpose of obtaining test-pieces after delivery shall be borne by the purchaser in the event of the test being satisfactory, and if unsatisfactory by the manufacturers, in a similar manner to that specified for the tests prior to delivery.

SPECIFICATION FOR FIRECLAY BRICKS, BLOCKS, TILES, ETC.

(Institution of Gas Engineers, 1934).

Definition.—This specification applies generally to goods made of fireclay and containing not more than 78 per cent. of silica. (For those richer in silica see p. 814.)

Refractoriness Safety Test.—Two grades of material are covered by the Specification:

(1) The No. 1 grade of material shows no "signs of fusion" when heated to Seger Cone 29 (about 1650° C.).

(2) The No. 2 grade of material shows no "signs of fusion" when heated to Seger Cone 26 (1580° C.).

The heating must take place in a suitable furnace at the rate of 50° C. per 5 minutes after 1000° C. has been reached. The test-pieces are tetrahedra with base-sides ¾ inch and a height of 1½ inches. The "signs of fusion" are described on p. 809.

Bricks which have a refractoriness equal to Cone 32 are regarded as "Special Refractory Materials" (p. 821).

Chemical Analysis.—A complete chemical analysis of the material is to be provided, when required by the purchaser, for his personal information only.

Surface and Texture.—The material shall be evenly burned throughout and of regular texture. All surfaces shall be reasonably true.

After-contraction or -expansion.—Two test-pieces, each 2½ inches to 3 inches by 1½ inches to 2 inches by 1½ inches to 2 inches with parallel ends, when heated slowly to 1410° C. in four hours, maintained at that temperature for two hours in an oxidising atmosphere and then allowed to cool, shall not show an average after-contraction or -expansion of more than

(i) 0·75 per cent. for No. 1 grade material,
(ii) 1·15 ,, ,, ,, No. 2 ,, ,,

with a tolerance of 0·1 per cent. for experimental error.

Variation from Specified Dimensions.—In ordinary bricks, 9 inches by 4½ inches by 2½ inches or 3 inches, there shall not be more than ± 1½ per cent. variation in length, +1½ to −2½ per cent. variation in width, and ± 2 per cent. variation in thickness. In special articles, the variation shall not exceed ± 2 per cent. from any specified dimensions.

The *jointing material* is to be quite suitable for use with the articles.

Crushing Strength.—The average crushing strength, when cold, shall be at least 1800 lbs. per square inch. The ends of the bricks shall be ground flat and parallel, and at least three whole bricks shall be tested in a vertical position.

Marking.—All bricks, blocks, or tiles shall be distinctly marked to show the grade to which they belong.

Inspection and Testing.—This clause is the same as that on p. 809.

GERMAN SPECIFICATIONS (1938).

The German Standard Specifications[1] are much too lengthy, even when summarised, to be included in this volume. They are as follows:—

Specifications relating to Shape.

DIN 1081 Full bricks, partial bricks and closers.

DIN 1082 Arch bricks.

DIN 1083 Cupola bricks.

Specifications relating to Quality.

DIN 1086 General properties and tolerances.

DIN 1087 Refractory bricks for furnaces and air-heaters (regenerators and recuperators).

DIN 1088 Refractory bricks for open-hearth steel-furnaces.

DIN 1089 Refractory bricks for coke ovens.

Other German Specifications, relating to modes of testing, sieves, etc., are also obtainable from the same publisher.

SPECIFICATION FOR FIRECLAY BRICKS

(U.S.A. Federal Specification HH—B—6716, 1936).

Fireclay bricks shall be of the following classes, as specified:—

Back-up Duty.—For structural use, as in exterior walls of boiler and other furnaces, where the brick does not come in direct contact with the heat.

Moderate Heat-duty.—For use at moderate temperatures, as in boilers operated at average ratings not exceeding 125 per cent. Resistance to spalling and slagging is important under these conditions of temperature.

Slag-resistant Duty.—For use under conditions where resistance to spalling is not of great importance and where resistance to slagging and high temperature is important. In general boiler practice, they may be used in the side walls, but if the refractories used are limited to one brand, material of either the intermediate or high heat-duty class is recommended.

Intermediate Heat-duty.—For use under conditions such as are encountered in general boiler practice with ratings from 125 to 250 per cent. and general incinerator practice. Resistance to slagging, spalling, and high temperatures is important.

High Heat-duty.—For use under fairly severe conditions of boiler and furnace practice, such, for example, as plant installations designed to operate

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[1] Obtainable from Beuth Verlag, Berlin, S.W.19.

at an average rating of not less than 250 per cent. High resistance to slagging, spalling, and to high temperatures is important.

Super-duty.—For use under extremely severe conditions, in oil-fired marine boilers and in certain installations where the use of bricks of unusually high resistance to spalling is of major importance, and where volume stability and resistance to temperature and slagging are also important.

The bricks and shapes covered by this Specification shall be compact, of homogeneous structure, free from checks, cracks, voids, or soft centre. All corners shall be sufficiently solid and strong to prevent excessive crumbling or chipping when handled.

All bricks of the standard 9-inch series and all special shapes shall not vary more than ± 2 per cent. from specified dimensions, covering both shrinkage and warpage, on dimensions of 4 inches or over. On dimensions under 4 inches, variations shall not exceed ± 3 per cent. Furthermore, the special shapes shall be free from such swells, warps, twists, or distortions as shall prevent ready and accurate laying up with a maximum joint of ⅛ inch.

Sampling.—Unless otherwise specified, fourteen 9-inch bricks shall be taken at random from every shipment of one carload or less and submitted for test. One half of these bricks shall be tested as required. If they fail to meet the requirements of a test (or tests) it shall constitute rejection. If the consignor desires a re-test, the test (or tests) in which the material failed shall be repeated, using the necessary numbers of bricks from the balance of the sample. If the material meets the requirements of a test (or tests) on the re-test, it shall constitute acceptance.

Bricks shall conform to the chemical and physical characteristics shown in the following table :—

Class or Duty.	P.C.E.,[1]		Quenching Test, not less than,	Silica-content,	Absorption,	Compressive Strength,	Linear Contraction,
	Seger Cone.	° C.	cycles.	per cent.	per cent.	lbs./in.^{2}	per cent.
Back-up . .	26	1595	0	..	..	[3] 3000	..
Moderate heat .	29	1640	5	..	..	..	..
Slag-resistant .	31	1680	5	..	[4] 10	..	..
Intermediate heat	31	1680	12	..	..	..	..
High heat . .	32	1700	18	[4] 65	..	..	..
Super-duty .	33	1745	[2] 18	..	..	..	[4] 1·0

Quenching Test.—The quenching test shall be conducted on standard 9-inch bricks. These bricks shall be placed without bond in the door of a furnace so that one end is exposed to atmospheric temperature and the other is flush with the inner wall of the furnace. For all classes of bricks, with the exception of the super-duty, the furnace is then brought to 1400° C. (2550° F. approximate equivalent) at a uniform rate in approximately 20 hours. For the super-duty class of bricks the end temperature is 1450° C. (2640° F. approximate equivalent) to be obtained in approximately 22 hours. In either case the final temperature is maintained for 5 hours and is measured by thermocouples flush with the inner face of the test-brick. The bricks should

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[1] Pyrometric cone equivalent (softening-point).

[2] After reheating at 1450° C. instead of at 1400° C.

[3] Minimum.

[4] Maximum.

not be removed until they have cooled to atmospheric temperature without induced draught.

The quenching is conducted in the following manner. The re-heated end of the brick is placed in the door of a suitable furnace maintained at 850° C. (1560° F. approximate equivalent) as indicated by the thermocouples placed close to and flush with the inner end face of the test-brick. The re-heated end of the brick should be flush with the inner face of the furnace and the outer end should be exposed to the free circulation of the air.

At hourly intervals, the heated end of the brick is immersed to a depth of 2 inches in running cold water for 3 minutes. The brick is then removed, allowed to steam in air for 5 minutes, and returned to the furnace door. This cycle is repeated until the specimen has failed or complied with the requirements.

The brick is considered to have failed when the entire plane surface of the heated end has completely spalled away. Pieces adhering to the test-end shall be removed when the structure has become so weakened that it will not support the weight of the brick when held either vertically or horizontally by the weakened portion.

The results on any one brand shall be reported as the average of five specimens.

Absorption.—The absorption shall be determined on bricks as received and without additional high-temperature heat-treatment in the laboratory.

The test shall be conducted on specimens not less than 100 g. in weight, one specimen to be taken from each of five bricks of any one brand and the average result reported.

The percentage absorption shall be determined according to the following formula:—

$$\text{Per cent. absorption} = \frac{W - D}{D} \times 100,$$

where W=weight of specimen after having been boiled in water for 2 hours and allowed to cool in the water;

D=weight of specimen after having been dried to constant weight at 110° C.

Compressive Strength.—The compressive strength shall be determined according to the American Society for Testing Materials, *Standard Method of Testing Brick,* Serial Designation C67–31.

Linear Change.—The linear change shall be determined according to the American Society for Testing Materials, *Standard Method for Permanent Linear Change after Reheating of Refractory Brick,* Serial Designation C113–36. Schedule C, which applies to the super-duty class of brick and which specifies reheating the brick at 1600° C. for 5 hours, shall be used.

That *simulative service tests,* together with the pyrometric cone equivalent and linear change test, may (at the discretion of the purchaser) replace all other tests specified for any one class of bricks.

Workmanship and pyrometric cone equivalent (softening-point) determinations shall be considered as control tests.

SPECIFICATION FOR CLAY-BONDED COKE OVEN BRICKS

(Heinrich Koppers G.m.b.H., Essen, 1938).

1. Only suitable raw materials to be used.
2. The materials must have a suitable composition, crushing strength, and refractoriness.

3. The silica-content shall be between 80 and 84 per cent.

4. The bricks must be accurate in shape and size, so that the joints do not exceed 3 to 4 mm.

The following tolerances are permitted:—

(*a*)	Dimensions up to 200 mm.	1 per cent.
(*b*)	„ between 200 and 400 mm.	2 „
(*c*)	„ above 400 mm.	3 „

The variations must be such that the brickwork as a whole is accurate in its dimensions.

5. The surface must be smooth and flat.

6. The bricks must emit a clear " ring " when struck.

7. The bricks must be free from cracks and hollows.

8. The arrises and corners must be complete and undamaged.

9. The after-contraction, after heating for 5 hours at 1400° C. and then cooling, must not exceed 1 per cent.

10. All bricks when heated to 1350° C. under a pressure of 2 kg. per sq. cm. must not shrink more than 2 per cent. in any dimension.

11. At least 70 per cent. of the samples must have a porosity of less than 28 per cent., and no sample must have a porosity greater than 30 per cent.

12. The crushing strength when cold must exceed 150 kg. per sq. cm.

13. The refractoriness of recuperator bricks is to be tested on a cylinder of 5 cm. diameter and 5 cm. height, which is maintained at the maximum specified temperature for one hour; after cooling, the shrinkage is measured.[1]

14. Specified conditions as to testing and sampling must be observed.

SPECIFICATION FOR SILICA BRICKS, BLOCKS, TILES, ETC.

(Institution of Gas Engineers, 1934).

Definition.—The material covered by this Specification is of two classes:

(1) That containing 92 per cent. or more of silica—known as " Silica Material."

(2) That containing between 78 and 92 per cent. of silica—known as " Siliceous Material."

Refractoriness Safety Test.—Test-pieces of the material of the same shape and size as those described on p. 809 and heated in the same manner shall have a refractoriness:

(1) not less than Seger Cone 30 (1670° C.) for silica material;

(2) not less than Seger Cone 29 (1650° C.) for siliceous material.

Chemical Analysis.—This clause is identical with that for fireclay bricks (p. 810).

Surface and Texture.—This clause is identical with that for fireclay bricks (p. 810).

After-contraction and -expansion.—This property is to be tested in the same manner as for fireclay bricks (p. 810), but with the following results:—

Silica material, after being heated to 1450° C., shall not show an after-expansion of more than 0·5 per cent. with a tolerance of 0·1 per cent. for experimental error.

Siliceous material, after being heated to 1410° C., shall not show an after-expansion or -contraction of more than 0·5 per cent. with a tolerance of 0·1 per cent.

Variations from Specified Dimensions.—There shall not be more than

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[1] The actual temperature is not stated.

1¼ per cent. variation in length, width, or thickness from the specified dimensions, except for dimensions less than 3 inches, when the permissible variation may be ± $\frac{1}{16}$ inch.

The *jointing material* is to be quite suitable for use with the articles.

Inspection and Testing.—This clause is the same as that on p. 809.

SPECIFICATION FOR SILICA BRICKS

(U.S.A. Federal Specification HH—B—681, 1933).

The material covered by this Specification is a brick of standard or special shape, which is composed of ground silica rock (quartzite or ganister) and a suitable binder and which has been burned to produce the desired strength and structure. The brick shall be free from checks, cracks, voids, or soft centres. All corners shall be sufficiently solid and strong to prevent excessive crumbling or chipping when handled. Such bricks are for foundry use and not for use in the fireboxes of boilers.

Composition.—Bricks shall contain not less than 95 per cent. total silica.

Softening Temperatures.—The pyrometric cone equivalent shall not be less than Cone 31 (approximately 3056° F. or 1680° C.). It shall be determined on part of the brick after grinding it to pass through a sieve with openings 0·208 inch wide. The powder is mixed with dextrin, glue, or other organic binder, moulded into "cones" 1 inch in height and baked at 1300° C. or below prior to testing.

The *apparent specific gravity* shall be not more than 2·38. It shall be determined on blocks 2·5×2·5×1·25 inches cut from three bricks so as to remove the original surface, using paraffin of known density for immersion at 25° C. Examination by petrographic microscope may be made in lieu of the specific gravity determination, to obtain information as to whether the silica bricks have been properly burned.

Dimension Tolerance.—Variations (plus or minus) of 2 per cent. from the specified dimensions covering both shrinkage and warpage shall be allowed on dimensions of 4 inches or over. On dimensions under 4 inches 3 per cent. shall be allowed.

Sampling.—Unless otherwise specified, six 9-inch bricks shall be taken at random from every shipment of 1 carload or less and submitted for tests. These bricks constitute a sample. One-half of the bricks of the sample shall be tested as required in this Specification. If they fail to meet the requirements of a test (or tests) it shall constitute rejection. If the consignor desires a re-test, the test (or tests) in which the material failed shall be repeated, using the necessary number of bricks from the balance of the sample. If the material meets the requirements of a test (or tests) on the re-test, it shall constitute acceptance.

SILICA BRICKS FOR COKE OVENS

(Heinrich Koppers G.m.b.H., Essen, 1938).

1. The quartzite of which the bricks are made must be clean and of suitable origin.
2. The material used for shaping the bricks shall contain 50 per cent. of particles less than 0·5 mm. and none larger than 5 mm.
3. The added lime shall not be less than 2½ or more than 3½ per cent. of the finished bricks.

4. The bricks must be burned at a temperature above 1400° C. for so long a time that an ample production of tridymite occurs.

5. The true specific gravity of the powdered bricks shall not exceed 2·38.

6. The porosity of the wall bricks must not exceed 25 per cent. and that of other bricks must not exceed 28 per cent.

7. The percentage of alumina and titanic oxide together in wall and burner bricks must not exceed 2 per cent.; that in other bricks must not exceed 3 per cent.

8. The refractoriness-under-load under a pressure of 2 kg. per sq. cm. must not be less than 1600° C. for wall and burner bricks, or 1500° C. for other bricks.

9. The bricks must be sufficiently accurate in shape to permit the joints to be less than 3 to 4 mm. wide. The following tolerances are permitted:—

(*a*)	Dimensions up to 200 mm.	1 per cent.
(*b*)	„ between 200 and 400 mm.	2 „
(*c*)	„ above 400 mm.	3 „

The variations must be such that the brickwork, as a whole, is accurate in its dimensions.

10. The bricks must not be distorted.
11. The bricks must emit a clear "ring" when struck.
12. The bricks must be free from cracks and hollows.
13. All arrises and corners must be complete and undamaged.
14. The specified conditions as to sampling and testing[1] must be observed.

PROVISIONAL SPECIFICATION FOR SILICA BRICKS FOR GLASSWORKS

(Society of Glass Technology, 1919).

At the desire of the purchaser, the following data shall be supplied for his personal information only, with average samples true to bulk:—

(*a*) Analysis.
(*b*) Refractoriness.
(*c*) Linear expansion after being heated to Cone 12.

1. *Chemical Composition.*—The bricks shall contain not less than 94 per cent. of silica and not more than 2 per cent. of lime.

2. *Refractoriness.*—Test-pieces shall not be more fusible than Cone 32 (about 1710° C.). The test shall be carried out in an oxidising atmosphere, the temperature of the furnace being increased at the rate of about 50° C. per five minutes.

3. *After-expansion.*—A test-piece after being heated to a temperature equivalent to Cone 12 for two hours shall not show, on cooling, more than 0·75 per cent. linear expansion.

4. *Texture.*—The bricks shall be uniformly burnt and shall have a regular texture with no holes or flaws.

5. *Variations from Measurements.*—All surfaces shall be reasonably true, and there shall not be greater variation than ± 2 per cent. from any specified dimension.

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[1] Not shown here.

SPECIFICATION FOR GLASS POT MATERIALS[1]

(Society of Glass Technology, 1919).

1. *Mixture.*—Clay mixture for pots shall consist of at least three portions—

(*a*) Bind clay.
(*b*) Base clay.
(*c*) Grog.

At the desire of the buyer, the following data shall be supplied with *samples true to bulk*:—

2. *Chemical Composition.*—The analysis shall show the content of silica, alumina, iron oxide, titanium oxide, lime, magnesia, potash, soda, and the loss on ignition.

3. *Fusion Test,* which shall record—

(i) Squatting temperature, measured by Seger cones, with the equivalents in ° C. and ° F.

(ii) Squatting temperature under load in ° C. and ° F. by standard test to be defined.

4. (*a*) *The bind clay* shall be a fat, plastic, weathered clay.

(*b*) *The base clay* shall be a highly refractory clay. Lumps shall be specially selected and hand-picked free from pyrites.

(*c*) *The grog* shall be prepared from well-burnt pieces of selected refractory clay. Burnt blocks shall show no signs of blue-stoning or black core. Nothing of the nature of ordinary firebricks shall be used for grog.

5. A sample of any portion when made up and fired to 1400° C. shall not show decided speckling due to iron in a segregated form.

6. A fracture of each portion when made up and burnt to 1400° C. shall show a dense structure, especially the bind clay. A wide range of vitrification is necessary without signs of over-firing.

7. Clay and grog shall be loaded in clean bags securely tied.

The committee urges that all care and supervision shall be exercised to see that the clays used are not contaminated with dirt or other foreign matter. Pans and mills should be thoroughly cleansed before use; where sieve bottoms are used, the pans should be swept out every day.

The committee believes that sufficient information exists to enable clays suitable for pots to be classified in three grades according to their composition and fusion temperature. The lowest, or Grade 3, corresponds with the material in general use; Grades 2 and 1 are purer and more refractory.

On p. 818 are tabulated limits for the composition and fusion temperature suggested in each grade. In each case, the compositions quoted are for fired samples.

TANK BLOCKS.[2]

At the request of the purchaser, the following data shall be supplied for his personal information only, together with average samples true to bulk:—

(*a*) Analysis, which shall show the content of silica, alumina, iron oxide, titanium oxide, lime, magnesia, potassium oxide, and sodium oxide.

(*b*) Refractoriness measured by Seger cones.

(*c*) Volume porosity.

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[1] This specification has not been widely adopted, as serious objections have been raised against it. See also W. J. Rees, *J. Soc. Glass Tech.*, 1930, **14**, Proc. 124.

[2] For the corresponding specification for silica bricks and cement see pp. 816 and 821.

(*d*) Linear contraction or expansion after being heated to a temperature equivalent to Cone 14.

(*e*) Crushing strength.

1. *Refractoriness.* Cones cut from blocks shall not be more fusible than Cone 30. The test shall be carried out in an oxidising atmosphere, the temperature of the furnace being increased at the rate of 50° C. per five minutes.

	Bind Clay.	Base Clay.	Grog.
Grade 3.			
Silica . . .	70 per cent. and under	70 per cent. and under	70 per cent. and under
Alumina . . .	25 „ and over	25 „ and over	25 „ and over
Ferric oxide . .	2·5 „ and under	2 „ and under	2 „ and under
Soda and potash .	2·5 „ „	1·8 „ „	1·8 „ „
Magnesia and lime .	1·0 „ „	1·0 „ „	1·0 „ „
Squatting temperature	Cone 28-29	Cone 30-31	Cone 31
Mechanical division .	12-mesh	12-mesh	10-mesh
Temperature of firing.	..	..	Cone 9 or above
Grade 2.			
Silica . . .	65 per cent. and under	60 per cent. and under	60 per cent. and under
Alumina . . .	30 „ and over	35 „ and over	35 „ and over
Ferric oxide . .	2 „ and under	2 „ and under	2 „ and under
Soda and potash .	2 „ „	1·8 „ „	1·8 „ „
Magnesia and lime .	1 „ „	0·6 „ „	0·6 „ „
Squatting temperature	Cone 30	Cone 32	Cone 32
Mechanical division .	50-mesh [1]	50-mesh	..
Temperature of firing.	..	..	Cone 12 or above
Grade 1.			
Silica . . .	60 per cent. and under	55 per cent. and under	50 per cent. and under
Alumina . . .	34 „ and over	40 „ and over	40 „ and over
Ferric oxide . .	1·8 „ and under	1 „ and under	1 „ and under
Soda and potash .	1·8 „ „	1·5 „ „	1·5 „ „
Magnesia and lime .	1·0 „ „	1·5 „ „	0·5 „ „
Squatting temperature	Cone 32	Cone 35	Cone 35
Mechanical division .	80-mesh [1]	80-mesh	12-mesh
Temperature of firing.	..	..	Cone 14 or above

[1] With less than 10 per cent. residue.

2. *Texture.*—The blocks shall contain no patches of ironstone or other segregated impurity. They shall be uniformly burnt throughout, and if any blue, black, or brown core is present, it shall be of the minimum extent practicable, having regard to the size of the block. The blocks shall be of regular texture and free from holes and flaws. The arrises shall be as reasonably sharp as is consistent with the size of the grog used. All surfaces shall be sufficiently true and plain as to permit all the blocks being walled together without appreciable joint space on the exposed face.

3. *Porosity.*—The volume porosity, that is,

$$\frac{\text{the volume of pores} \times 100}{\text{volume of piece (including pores)}},$$

shall not exceed—

For flux-line blocks	18 per cent.
„ replacement flux-line blocks . .	23 „
„ bottom side blocks . . .	25 „
„ tank bottom blocks . . .	30 „

4. *After-contraction or After-expansion.*—Test-pieces (about 3 inches in length and 1 to 2 inches in depth and breadth) taken from any portion of the blocks after being heated to and maintained for two hours at a temperature equivalent to Cone 14, shall not show, when cold, more than 2 per cent. linear contraction or expansion. When the test temperature has been reached, the furnace shall be maintained constant throughout the test period.

5. *Crushing Strength.*—The blocks shall be capable of withstanding a crushing strain of not less than 1600 lbs. per square inch. The portion of the block tested shall be a 4-inch cube, and shall have the two ends which come in contact with the jaws of the machine ground or sawn flat, and made truly parallel by facing with plaster of Paris in the usual way.

6. *Inspection and Testing.*—The purchaser or his representative shall have access to the works of the maker at any reasonable time, and shall be allowed to inspect the blocks before delivery. Duplicate test-pieces representative of the bulk of the material ordered shall be selected prior to delivery. The cost of the blocks damaged for the purpose of obtaining the test-pieces shall be borne (*a*) by the purchaser when the material is proved satisfactory; (*b*) by the maker if unsatisfactory.

Recommendations—

(*a*) The committee suggests that the clay aggregate for tank blocks should usually consist of three portions—

1. Bind clay, which should be a fat, aluminous clay.
2. Base clay, which should be a strong, refractory clay.
3. Grog, which should consist of bind and base clays mixed together in the finely ground state, tempered, and burned at Cone 14.

(*b*) The following compositions and properties are suggested as indicating suitable clays:—

Bind Clay.	Composition after Burning.
Free silica	In small proportions only.
Alumina	36 to 40 per cent.
Total alkalies . . .	Less than 2·5 per cent.
,, fluxes . . .	,, 4·5 ,,

It should have a low sintering temperature, but should not be more fusible than Cone 31.

Base Clay.	Composition after Burning.
Alumina	25 to 32 per cent.
Total alkalies . . .	Less than 1·4 per cent.
,, fluxes . . .	,, 4·0 ,,

It should not be more fusible than Cone 31.

(*c*) The following notes are suggestions as to suitable mixtures and methods for the consideration of tank block manufacturers:—

(i) *Tank bottoms*—

Fat, plastic clay, 1 volume.
Lean or strong clay, 3 volumes.

These clays should be well mixed in the dry, ground condition.

Grog should always be made by tempering a portion of the above mixture, making it into slabs (say 12 inches by 12 inches by 4 inches), and burning to Cone 10. The fired slabs should be crushed in a type of crushing machine producing sharp-edged grains with a minimum of fine material.

Mixture for blocks—

Dry, ground clay of above mixture, 5 volumes.
Grog passing $\frac{1}{4}$-inch mesh and held by $\frac{1}{8}$-inch mesh, 1 volume.
,, ,, $\frac{1}{8}$-inch ,, ,, $\frac{1}{16}$-inch ,, 1 ,,
,, ,, $\frac{1}{16}$-inch ,, ,, $\frac{1}{32}$-inch ,, 1 ,,

These constituents should be well mixed dry, tempered by the addition of the minimum quantity of water, pugged well or treated in a pan mill with the rolls raised, and then allowed to mature for one month at least.

Blocks should be slowly dried and burned to Cone 10.

(ii) *Bottom side blocks—*

Fat, plastic clay, 2 volumes.
Lean or strong clay, 2 volumes.

Grog should be made from the above mixture (as for bottom blocks) and burned to Cone 12.

Mixture for blocks—

Dry, ground clay of the above mixture, 5 volumes.
Grog passing $\frac{1}{6}$-inch mesh and held by $\frac{1}{8}$-inch mesh, 1 volume.
,, ,, $\frac{1}{8}$-inch ,, ,, $\frac{1}{16}$-inch ,, 2 volumes.
,, ,, $\frac{1}{16}$-inch ,, ,, $\frac{1}{32}$-inch ,, 1 volume.

Blocks should be burned to Cone 12.

(iii) *Top side (flux-line) blocks—*

Fat, plastic clay, 2 volumes.
Strong clay, 1 volume.

Grog should be made by burning the above mixture to Cone 14.

Mixture for blocks—

Dry, ground clay of the above mixture, 5 volumes.
Grog passing $\frac{1}{8}$-inch mesh and held by $\frac{1}{10}$-inch mesh, 1 volume.
,, ,, $\frac{1}{10}$-inch ,, ,, $\frac{1}{32}$-inch ,, 2 volumes.

Blocks should be burned to Cone 14.

(iv) *Replacement (flux-line) blocks—*

Fat, plastic clay, 1 volume.
Lower-grade [1] fat clay, 1 volume.
Strong clay, 1 volume.

Grog should be made by burning the above mixture to Cones 6 to 8.

Mixture for blocks—

Dry, ground clay of the above mixture, 5 volumes.
Grog passing $\frac{1}{6}$-inch mesh and held by $\frac{1}{8}$-inch mesh, 2 volumes.
,, ,, $\frac{1}{8}$-inch ,, ,, $\frac{1}{16}$-inch ,, 2 ,,
,, ,, $\frac{1}{16}$-inch ,, ,, $\frac{1}{32}$-inch ,, 1 volume.

Blocks should be burned to Cones 6 to 8.

[1] *A suitable lower-grade plastic clay* should contain when fired—
Alumina, 34 to 38 per cent.
Alkalies, not above 3 to 5 per cent.
Total fluxes, not above 6·5 per cent.
It should have a low sintering temperature, and should not be more fusible than Cone 26.

PROVISIONAL SPECIFICATION FOR SILICA CEMENT FOR GLASSWORKS

(Society of Glass Technology, 1919).

Silica cement shall, in all cases, be finely ground, and suitable for binding together the bricks for which it is supplied. It shall contain not less than 92 per cent. of silica, and shall be capable of withstanding the same test for refractoriness as the brick.

SPECIFICATION FOR SPECIAL REFRACTORY MATERIALS

(Institution of Gas Engineers, 1934).

Bricks and other articles made of fireclay with a refractoriness equal to or greater than Seger Cone 32 are regarded as " Special Refractory Materials," and so are those made of chromite, sillimanite, corundum, carborundum and other electrically fused materials.

No standard specification has been issued, but it is suggested that the variations from specified dimensions should not exceed those for silica bricks (p. 814).

SPECIFICATION FOR SILICA CEMENT

(U.S.A. Federal Specification HH—C—176, 1933).

The material covered by this specification is a heat-resistant cement composed of ground silica brick-bats and/or ground silica rock (quartzite) with sufficient siliceous fireclay to make a smooth-working mortar when tempered with water. It is not to be used with fireclay bricks.

Composition.—The cement shall contain not less than 88 per cent. total silica (SiO_2).

Softening Temperature.—The pyrometric cone equivalent shall not be less than Cone 26 (approximately 2903° F., or 1595° C.).

Fineness.—The cement shall be air-dry, and not less than 99 per cent. of it shall pass through a United States standard sieve No. 30.

SPECIFICATION FOR PLASTIC FIRECLAY

(U.S.A. Federal Specification HH—R—191, 1936).

The material covered by this specification includes a mixture of grog, water, and raw clay as well as clay alone. It is specially suitable for those parts of furnaces where special fireclay shapes have been used, and is also recommended for constructing small furnaces.

Silica-content.—The material shall contain not more than 65 per cent. total silica (SiO_2) calculated on the dry weight.

Pyrometric Cone Equivalent (softening-point).—The pyrometric cone equivalent shall not be less than Cone 31 (approximately 3056° F. or 1680° C.).

Water-content.—The material as delivered shall contain not more than 15 per cent. water calculated on the plastic weight.

Shrinkage.—The combined linear drying- and burning-shrinkage, after being heated for 5 hours at 1400° C., shall not exceed 4 per cent. of the plastic length.

SPECIFICATION FOR REFRACTORY SILICA CEMENT

(Heinrich Koppers G.m.b.H., Essen, 1938).

Composition.—The composition of the cement should be similar to that of the bricks for which it is used. It should contain not less than 90 per cent. of silica, and only so much clay as is necessary for satisfactory manipulation.

Refractoriness.—The test for refractoriness is carried out as follows: Two test-bodies (50 mm. in diameter and 50 mm. high) are built together with a 10 mm. joint, and when the joint has matured the test-piece is heated to and maintained at an agreed temperature under a load of 2 kg./cm.^{2} for an agreed time. No reduction in the height of the test-piece should occur. No alteration of the jointing material must take place.

Refractory cement for use in gas producers or generators should form a strong joint at a low temperature. For other purposes, and with such refractory materials as sillimanite, the cement used should be made largely of the same material—the properties of which must be in accordance with the corresponding specifications.

APPENDIX.

COMPARISON OF SEGER CONES AND TEMPERATURES.

(BASED ON THE DETERMINATIONS BY SIMONIS IN 1908.)

Seger Cone.	Temperature.		Seger Cone.	Temperature.		Seger Cone.	Temperature.	
	° C.	° F.		° C.	° F.		° C.	° F.
022	600	1112	02a	1060	1940	19	1520	2768
021	650	1202	01a	1080	1976	20[1]	1530	2786
020	670	1238	1a	1100	2012	26	1580	2876
019	690	1274	2a	1120	2048	27	1610	2930
018	710	1310	3a	1140	2084	28	1630	2966
017	730	1346	4a	1160	2120	29	1650	3002
016	750	1382	5a	1180	2156	30	1670	3038
015a	790	1454	6a	1200	2192	31	1690	3074
014a	815	1499	7	1230	2246	32	1710	3110
013a	835	1535	8	1250	2282	33	1730	3146
012a	855	1571	9	1280	2336	34	1750	3182
011a	880	1616	10	1300	2372	35	1770	3218
010a	900	1652	11	1320	2408	36	1790	3254
09a	920	1688	12	1350	2462	37	1825	3317
08a	940	1724	13	1380	2516	38	1850	3362
07a	960	1760	14	1410	2570	39	1880	3416
06a	980	1796	15	1435	2615	40	1920	3488
05a	1000	1832	16	1460	2660	41	1960	3560
04a	1020	1868	17	1480	2696	42	2000	3632
03a	1040	1904	18	1500	2732			

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[1] The numbers 21 to 25 are not manufactured, as their fusing-points lie too close together and their indications are irregular.

The temperatures indicated by Seger cones only agree with those in the table when the cones are heated sufficiently slowly in an oxidising atmosphere. If unburned or incompletely burned gas (reducing conditions) is present, some of the cones become altered externally and do not bend, even at a far higher temperature than that at which they are supposed to do so.

HOLDCROFT'S THERMOSCOPE BARS.

(Approximate Bending Temperatures.)

Bar No.	Temperature.		Bar No.	Temperature.	
	°C.	°F.		°C.	°F.
1	600	1112	22	1080	1976
2	650	1202	23	1100	2012
3	670	1238	24	1120	2048
4	700	1292	25	1140	2084
5	730	1346	26	1200	2192
6	760	1400	26*a*	1230	2246
7	790	1454	27	1250	2282
7*a*	810	1490	27*a*	1270	2318
8	840	1544	28	1280	2336
9	860	1580	29	1300	2372
10	875	1606	30	1325	2415
11	890	1634	31	1350	2462
12	905	1660	32	1380	2516
13	920	1688	33	1430	2606
14	935	1715	34	1460	2660
15	950	1742	35	1475	2688
16	960	1760	36	1490	2714
17	970	1778	37	1505	2740
18	985	1806	38	1520	2768
19	1000	1832	39	1535	2796
20	1040	1904	40	1550	2823
21	1060	1940			

COLOUR OF FIREBRICKS AT VARIOUS TEMPERATURES.

If firebricks are placed in a darkened chamber, such as a kiln, and heated their " colour " will approximately indicate their temperature as follows :—

Earliest visible red	500–650° C.
Dull red	700–800° C.
Cherry red	850–900° C.
Full red	900° C.
Bright red	1000° C.
Orange	1100° C.
Bright orange or yellow	1200° C.
White	1500° C.
Dazzling white	1600° C.
Firebricks begin to lose shape	1600°–1800° C.

WORKING TEMPERATURES.

The following temperatures are the highest reached in normal working. Owing to differences in the materials treated and in local conditions, the figures are only approximate, and wide departures therefrom occur in some works.

	° C.
Annealing furnaces (metals)	800–1500
Blast-furnaces: at tuyère	1900–2000
,, ,, tapping	1550–1600
,, ,, regenerators	1100–1200
Boilers: combustion chamber	1250
,, setting	1100
Brass-melting furnaces	1200
Calcining furnaces for bauxite	1500
,, ,, ,, magnesite	1700
Chemical furnaces	700–1200
Chimney base	350–1250
Coke ovens: chambers	1100
,, ,, regenerators	1200
Converters	1500–1650
Crucible furnaces	1450–1600
Cupola furnaces	1100–1500
Gas producers	700–1300
Glass furnaces: refining pots	1200–1300
,, ,, annealing	400– 600
,, ,, tanks	1200–1320
Hearths	900–1400
Kilns: burning bauxite bricks	1500
,, ,, cement	1400–1600
,, ,, chromite bricks	1450
,, ,, crucibles	1000–1300
,, ,, fireclay bricks	1250–1500
,, ,, glass pots	1100
,, ,, grog	1350–1500
,, ,, lime	900–1200
,, ,, magnesia bricks	1400–1500
,, ,, porcelain	1300–1500
,, ,, retorts	1150–1500
,, ,, saggars	1200–1350
,, ,, silica bricks	1200–1500
Kilns: frit	1100–1400
Open-hearth furnace during boiling	1600
,, ,, ,, tapping	1650
Regenerators—gas leaving	1200
Retort settings	1200
Reverberatory furnaces	900–1400
Steel-melting in crucibles	1450–1500

INDEX.

N.B.—Greek letters are treated as if replaced by the corresponding lette alphabet.

PRINTED IN GREAT BRITAIN BY NEILL AND CO., LTD., EDINBURGH.