OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

FAIR USE POLICY

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

C 5431

cK

Distr.
LIMITED

ID/WG.179/3
26 April 1974

ORIGINAL: ENGLISH

United Nations Industrial Development Organization

In-Plant Training Workshop on
the Production of Refractories

Pilsen, Czechoslovakia

11 - 28 June 1974

RAW MATERIAL REQUIREMENTS FOR THE VARIOUS TYPES OF REFRACTORIES [1]

Rex W. Grimshaw *

---

* Department Mining and Mineral Sciences, The University, Leeds, England

[1] The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

Distr.
LIMITED

ID/WG.179/3 SUMMARY
26 April 1974

ORIGINAL: ENGLISH

United Nations Industrial Development Organization

In-Plant Training Workshop on
the Production of Refractories

Pilsen, Czechoslovakia

11 - 28 June 1974

RAW MATERIAL REQUIREMENTS FOR THE VARIOUS TYPES OF REFRACTORIES [1]

Rex W. Grimshaw *

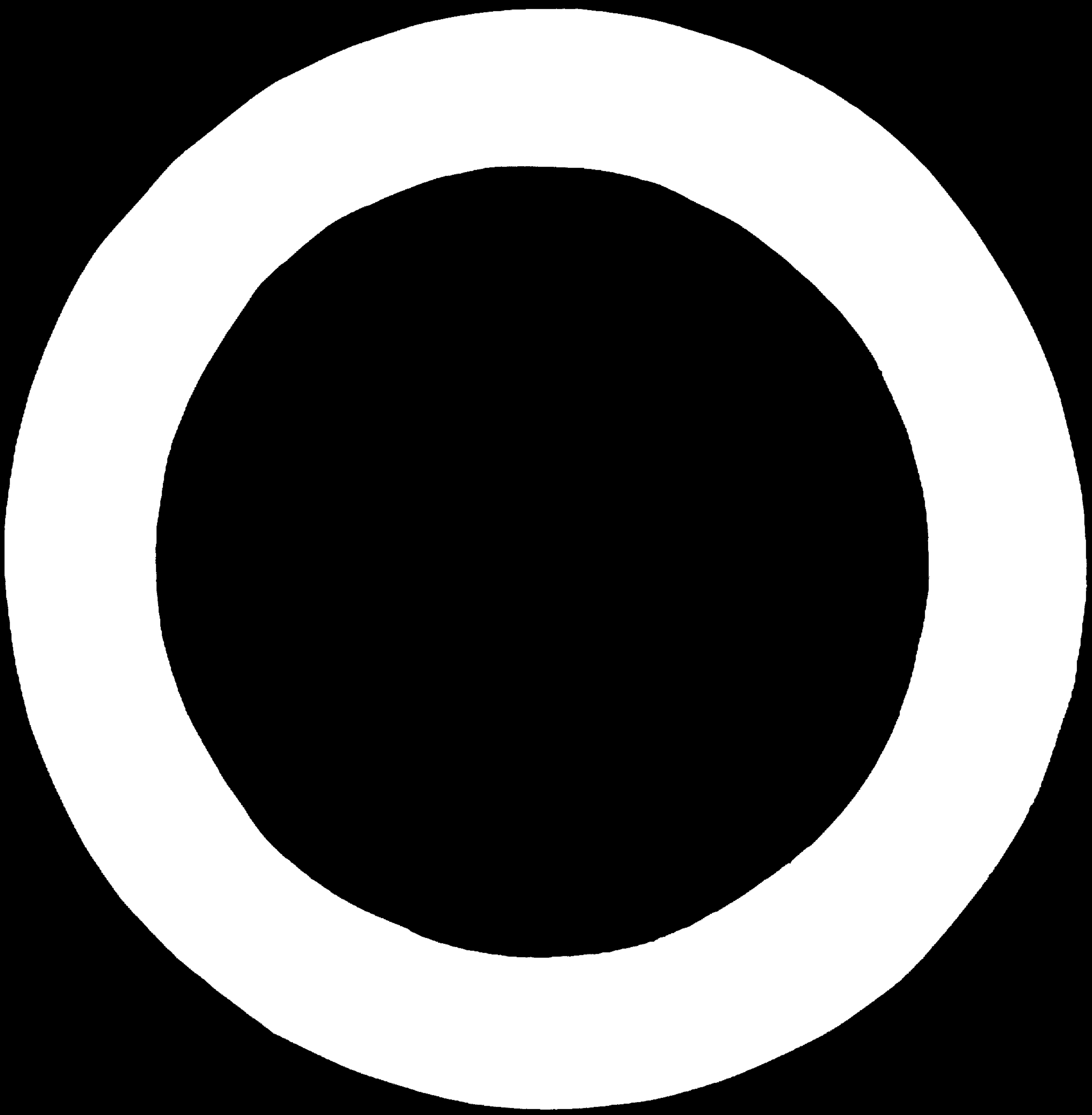
SUMMARY

---

* Department Mining and Mineral Sciences, The University, Leeds, England

[1] The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

id.74-2588



This publication is concerned principally with the raw materials required for the manufacture of refractories essential to the various industries which use high temperature processes.

Four main groups are considered, namely the alumino-silicates, the basics range, monolithic compositions and special refractories.

The alumino-silicates range from virtually pure alumina to pure silica and they include the important mullite and calcined kyanite class and also refractory clays.

It is in basic refractories that the most important technical advances have been made in recent years. The use of high purity magnesias and dolomites and their conversion into products of high density and hardness has led to qualities able to withstand the demands of the new oxygen-enriched steel-melting processes.

Monolithic refractories, particularly castables and mouldables, have found favour in recent years largely because of their cheapness and greater ease of installation over conventional brick shapes. The important requirements of these classes of refractory are detailed, as also are the specifications of each type.

Special refractories are considered both in terms of new materials such as zircon, beryllia, etc., and of techniques of manufacture such as fusion-casting, fibre formation and the production of insulating bodies.

The important uses of refractories have been described in the context of acceptable chemical and mineralogical compositions. Alternative materials, their implications both economically and technologically, and their potential use in developing countries have been given due consideration.

Distr. LIMITADA
ID/WG.179/3 SUMMARY
26 abril 1974

ESPAÑOL
Original: INGLES

Organización de las Naciones Unidas para el Desarrollo Industrial

---

Curso práctico de capacitación en el trabajo
sobre fabricación de productos refractarios

Pilsen (Checoslovaquia)

11 - 28 junio 1974

MATERIAS PRIMAS NECESARIAS PARA LOS DIVERSOS TIPOS DE PRODUCTOS REFRACTARIOS[1]

Rex W. Grimshaw*

RESUMEN

La monografía que aquí se resume trata principalmente de las materias primas necesarias para la manufactura de materiales refractarios cuya utilización es esencial para las diversas industrias que emplean procesos de fabricación con temperaturas elevadas.

Se examinan cuatro grupos principales, a saber: los aluminosilicatos, la gama de materiales refractarios básicos, las composiciones monolíticas y los materiales refractarios especiales.

Los aluminosilicatos abarcan desde la alúmina prácticamente pura hasta la sílice pura, y se cuentan entre ellos los pertenecientes a la importante clase de la mullita y de la cianita calcinada, así como las arcillas refractarias.

---

* Departamento de Minería y Mineralogía, Universidad de Leeds (Inglaterra).

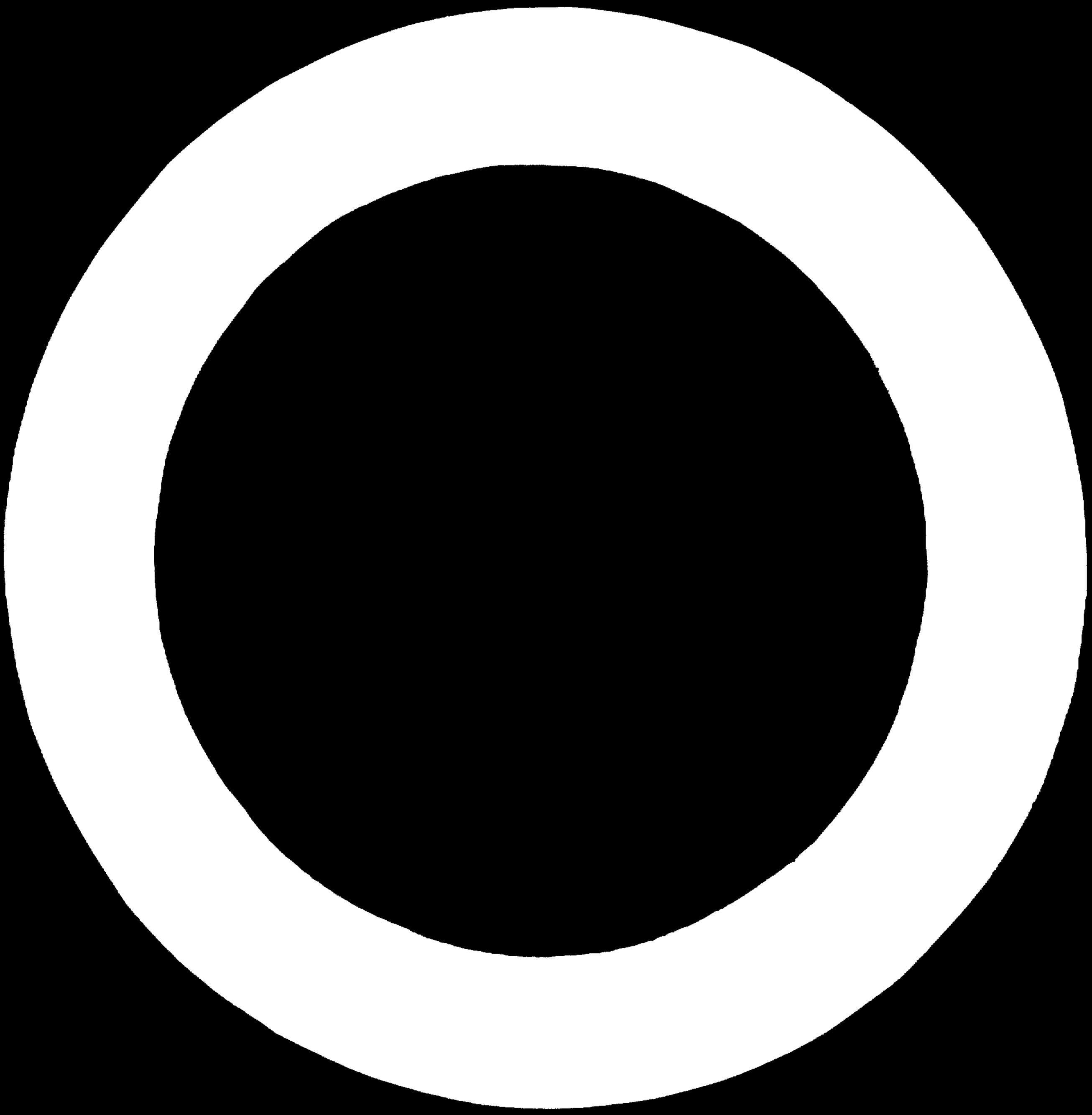
[1] Las opiniones que el autor expresa en este documento no reflejan necesariamente las de la Secretaría de la ONUDI. La presente versión española es traducción de un texto no revisado.

En la esfera de los materiales refractarios básicos es donde se han registrado los progresos técnicos más importantes en los últimos años. La utilización de magnesias y dolomitas de gran pureza, y su conversión en productos de alta densidad y dureza, ha permitido conseguir productos capaces de satisfacer las exigencias de los nuevos procesos de obtención de acero al oxígeno.

Los materiales refractarios monolíticos, en particular los compuestos moldeables, tienen mucha aceptación en los últimos años, debido principalmente a su bajo costo y a que son más fáciles de instalar que los ladrillos de formas convencionales. Se pormenorizan los requisitos importantes aplicables a estas clases de materiales refractarios, así como las especificaciones correspondientes a cada tipo.

Los materiales refractarios especiales se examinan tanto desde el punto de vista de los nuevos materiales -el zirconio, la berilia, etc.- como de las técnicas de manufactura, por ejemplo, el colado por fusión, la formación de fibras y la producción de materiales aislantes.

Las aplicaciones importantes de los materiales refractarios se han expuesto en el marco de composiciones químicas y mineralógicas aceptables. También se han tenido debidamente en cuenta otros posibles materiales, así como las consecuencias económicas y tecnológicas de su utilización, y las posibilidades existentes al respecto, en los países en desarrollo.



CONTENTS

I. NATURE OF REFRACTORY MATERIALS.

Many industrial processes involve high temperatures. The function of refractories is to contain the heat and the materials which are being heated. Although the ability to withstand heat without melting or deforming is a prime requirement of refractory materials, other characteristics are frequently important. These include resistance to erosion and corrosion by gases, liquids and dusts, the ability to withstand sudden changes in temperature and specific thermal-insulation properties.

The principal application of refractory materials is in the iron and steel industries. Temperatures of up to 1700°C are frequently involved and often corrosive dusts, molten slags and metals have to be contained in and transported through resistant materials. The melting and heating units are usually of large size so that refractories are required in large tonnages. Frequent replacement and relining is necessary. Suitable refractory materials must therefore be available in quantity and they must be relatively cheap and easy to fabricate,sometimes into highly complex shapes.

The refractory materials of commerce are mostly confined to naturally-occurring minerals. With the exception of elemental carbon - in the form of graphite - these may be regarded as oxides or mixed oxides of some of the more common elements of the Periodic Table.

Table 1 shows the melting point of the important oxides which are to be found in refractory materials.

When two or more oxides are present in a mineral form either as mixtures or as compounds, some melting will usually occur at temperatures below the melting point of the individual components. A combination of strongly acidic and alkali oxides can produce very low melting point mixtures and alkali oxides are particularly troublesome impurities, especially in siliceous mixtures.

Table 1. The Melting Point of Important Oxides Found in Refractory Materials.

Period I	Li_2O 1700°C	BeO 2570°C	B_2O_3 577°C			
Period II	Na_2O 1275	MgO 2820	Al_2O_3 2050	SiO_2 1728°C		
Period III	K_2O 430	CaO 2572	Sc_2O_3 2430	TiO_2 1850	Cr_2O_3 1970°C	$Fe_2O_3(FeO)$ 1210°C
Period IV		SrO 2430	Y_2O_3 2410	ZrO_2 2720		
Period V		BaO 1923	La_2O_3 2315	ThO_2 2470		

The oxides quoted in Table 1 include those which occur most commonly in surface minerals and rocks. Some of these have a high melting point thus enabling a wide range of refractory materials to be manufactured. The alkaline earth oxides, particularly magnesia, are chemically basic in addition to possessing a high melting point; these are most valuable in steel-manufacturing processes where basic slags and dusts pose additional hazards in the melting operation. On the other hand, silica, derived from natural quartz or related minerals, is an acidic refractory capable of resisting iron oxide and similar dusts. Alumina and alumino-silicates are also refractory combinations of great value in industrial installations.

In large scale applications, it is customary to use refractory materials which are commonly occurring and which do not require much beneficiation from their natural form. As high temperature technology advances, however, there is an ever-increasing demand for refractories capable of withstanding extreme conditions of temperature, stress and corrosion. For these purposes special oxide compositions are finding favour; these include zircon and zirconia, beryllia, rare earth oxides, thoria, oxides of uranium and several others. In this same category may be included some synthetic species such as carbides and nitrides of silicon, boron and tungsten, all of which combine excellent refractory qualities with other important properties such as hardness and thermal shock resistance. Refractory metals of which molybdenum and tungsten are excellent examples are also being used for specialist applications.

Refractories thus cover a wide range of raw materials and product applications. From several points of view, however, it is convenient to consider them under four main groupings. These are:

i) The alumino-silicate range, extending from high-purity aluminas to silica bricks containing +99% SiO_2 and embracing the important fireclay, siliceous, and kyanite groups.

ii) Basic refractories including magnesia, chrome magnesites, dolomites, forsterites, etc.

iii) Mouldable and castable compositions which differ from the previous two groups in that they are applied as coatings or gunned or rammed structures as opposed to fired bricks and shapes.

iv) Special compositions either in bricks, shapes or monolithic form.

Refractory materials are defined as substances which have the capacity to withstand high temperatures without undue melting, shrinkage or distortion. Although there is no definite stipulated lower limit, a softening point of 1500°C is usually regarded as a minimum and some materials melt in excess of 3000°C. Because of the complexity of composition of most refractory materials, they do not have a definite melting point, but a range of temperature over which they become progressively softer. For this reason, the refractoriness is defined in arbitrary values assessed on the equivalent performance of standard cones on a rising temperature test. A cone value, based on Seger, Orton or similar standards is frequently quoted and the equivalent melting temperature assessed from tables.

Although a refractory material is usually defined and classified in terms of its melting characteristics, other properties may be of greater importance. In large industrial furnaces where high stresses are frequently encountered it is the refractoriness-under-load which may be of the greatest significance. Metal-melting furnaces need to be lined with refractory material capable of resisting erosion and corrosion by molten metals and slags. In other applications, an ability to prevent the escape of gases or to retain heat, necessitates close textural control of the refractories. Thermal shock resistance or the capacity to withstand fluctuations in temperature can have considerable significance in some instances. These and several other properties frequently need to be taken into account in selecting suitable refractory materials for use in particular applications.

Refractory materials are not only diverse in chemical and mineralogical compositions, they also embrace a wide range of shapes and sizes. The unit most widely employed is the standard modular brick, rectangular in shape, but end and side wedges and bricks elongated or tapered in one or more dimensions are commonly required. Massive blocks with dimensions greater than 12 ins. are necessary for certain applications. The user industries call for a wide range of special shapes, often of intricate design. Trumpets, runners, nozzles, spouts, checkers are but a few essential shapes to the steel and other industries. Modern high temperature technology often involves structures so complex that conventional pre-fired refractory shapes cannot be incorporated; for such purposes, castable mixtures and ramming compositions have been developed and these are now widely employed.

It must be accepted that some refractory products call for such sophisticated manufacturing techniques and raw materials that high technical skills are essential. However, by far the greater tonnage of refractory materials needs relatively cheap and easily accessible minerals which can be manufactured by standard and versatile machinery. Experienced management coupled with careful workmanship can produce an acceptable quality capable of meeting most of the demands of industries which involve high temperatures.

It is not possible to present accurate figures for the tonnages of refractories of the various types which are required by a particular country. So much depends on the methods used in the various high temperature industries and their output.

If a steel industry is established, it will be the biggest user of refractories by far and the associated iron-making and foundry practice will also be large consumers.

Table 2 shows a simplified summary of the U.K. utilisation of refractories in 1970.

Table 2. Calculated Usage of Refractories in U.K. (1970).

Industry.	Type of refractory used (tonnage in m.tons x 10^3)		
	Alumino-Silicate	Basics	Monolithics
Steel-making	633	176	224
Iron-making	118	-	42
Foundries	31	13	54
Ceramics	73	6	13
Cement	10	14	2
Glass	29	3	4
Others	61	21	14
Totals	955	233	353

The British steel industry produced 27.6 x 10^6 m.tons in 1970. Countries with a greater proportion of basic oxygen vessels for steel production would use considerably less refractories per ton steel, particularly those of the alumino-silicate type, but the consumption of monolithics would be likely to show a substantial increase.

II. ALUMINO-SILICATE RANGE OF REFRACTORIES.

On a tonnage basis, over 70% of all refractories used in industrial practice are of the alumino-silicate type. If the grogs used in castable and mouldable compositions are also taken into account the figure is even higher.

Alumino-silicates are the most prolific of the earth's surface rocks. Several species are of high refractoriness and the clay varieties are easy to mould by simple techniques into dense refractories of standard or complex shapes.

The end members of the series alumina and silica have melting points of 2130°C and 1730°C respectively. The two components form a eutectic system but in the absence of other components the minimum point at which liquid can occur is 1595°C at a <u>weight</u> composition of 9% Al_2O_3 and 91% SiO_2.

The phase equilibrium diagram of the two components (Figure I) shows the main features of alumino-silicate refractories. High alumina compositions consist predominantly of corundum (α-alumina) but as the silica content is increased the mineral mullite $3Al_2O_3.2SiO_2$ becomes the major crystalline phase. Mixtures in the silica-rich section of the equilibrium diagram contain cristobalite, the high temperature crystal modification of pure silica.

These same crystalline modifications are to be found in the commercial refractories manufactured from natural alumino-silicate minerals and the refractoriness of these products shows the same general trend of the theoretical diagram (Figure II). This is all the more surprising because the commercial refractories contain impurities which cause liquid to develop at low temperatures tending to reduce the melting point.

It is mainly the alumina-silica ratio which determines the refractoriness of this class of materials but it is implicit that to be suitable as refractories, only minimal quantities of alkalies, iron oxide and other impurities can be permitted.

The refractoriness of a wide range of alumino-silicates can be calculated from the chemical composition by a technique attributed to Ludwig. From a chemical analysis of calcined material the molar ratios of each oxide component are calculated. The composition is then represented as a molecular formula in which the proportion of Al_2O_3 is taken as unity. The general formula is:

$$x(R_2O + RO).\ Al_2O_3.ySiO_2$$

R_2O is the molar percentage of alkali oxides Na_2O and K_2O.

RO is the molar percentage of divalent oxides such as

CaO, MgO and FeO (iron oxide should be calculated as FeO).

Titania (TiO_2) is included with SiO_2.

From the formula calculated in this way, graphs can be compiled relating the refractoriness to the alumina:silica ratio and the content of fluxing oxides. Figure III is a chart in which x in the formula is the vertical and y the horizontal axis. Iso-refractory lines corresponding to various Seger cones can be drawn from prior experimentation and hence the refractory value of any composition ascertained with a fair degree of accuracy. At all $Al_2O_3:SiO_2$ ratios, approximately 1.3% by <u>weight</u> of Na_2O reduces the refractoriness by about one cone value (20–30°C).

Alumino-silicate refractories may be sub-divided into various categories depending mainly on their composition.

High Aluminas.

Refractory compositions containing more than 98% Al_2O_3 by weight belong to the field of special ceramics. They have a limited but important use in

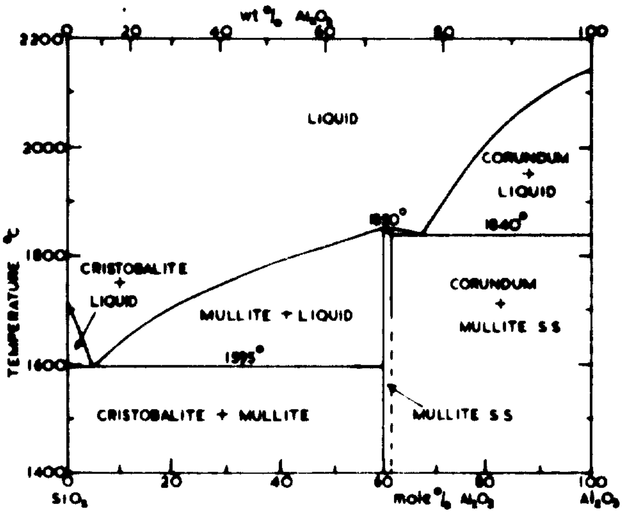


Figure I. Phase equilibrium diagram of Al_2O_3/SiO_2.

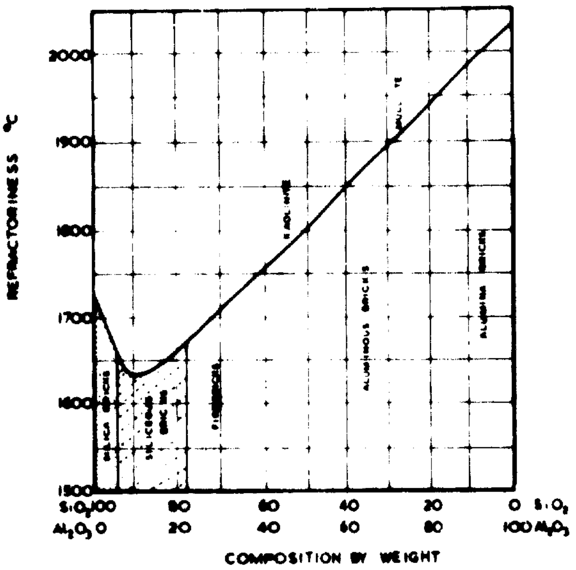


Figure II. The refractoriness of commercial alumino-silicate materials.

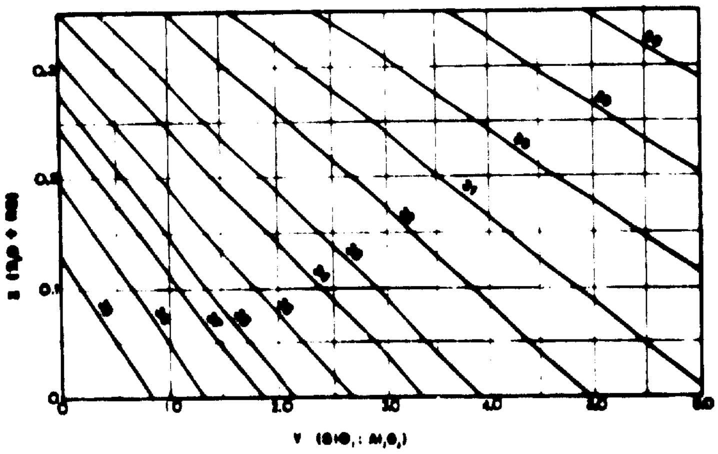


Figure III. Ludwig's Chart.
Equivalent cone values in °C: 39-1880; 38-1850; 37-1825; 36-1790; 35-1770; 34-1750; 33-1730; 32-1710; 31-1690; 30-1670; 29-1650; 28-1630.

that they can withstand temperatures in excess of 1800°C and also a wide range of erosion and corrosion conditions. Refractories of this excellence are usually manufactured by sophisticated techniques from extremely pure raw materials; they are dense - some are completely non-porous to gas - so they are formed by high pressure methods and fired to a temperature at which sintering or partial fusion occurs (+ 1750°C). Some are actually formed by fusion methods.

The raw materials for this class of product are derived from bauxites but only after they have been purified to Bayer alumina by intense chemical means. The almost-pure trihydrate of alumina is then calcined and heated to produce a dense aggregate known as sintered alumina. Tabular alumina is another very pure, highly calcined form of alumina which is most valuable in special refractory compositions; it is +99.5% Al_2O_3.

High alumina compositions are hard, resistant to erosion and to many corrosive materials and of high refractoriness. These are used as furnace linings, as runners and nozzles for a variety of industrial processes.

Alumina Refractories.

Alumina refractories may be defined as those containing not less than 88% Al_2O_3 by weight. They are manufactured from bauxites which are low in iron oxide content.

Bauxite is the general name given to lateritic-type of formations in which hydroxides of alumina predominate. In most bauxites, the trihydroxide of alumina, gibbsite $Al(OH)_3$ is the predominant type but occasionally the monohydroxide, diaspore $AlO.OH$ is to be found.

The most common use of bauxite is in the manufacture of aluminium but the ore is a valuable refractory raw material, particularly when the iron oxide content is low (less than 2%). Unfortunately bauxites of this quality are rare and extensive occurrences are available only from Guyana and China at the present time.

The chemical requirements for a bauxite suitable for refractory quality is as follows; the values are calculated on a calcined basis.

Al_2O_3	85 - 95%	CaO	0.0 - 1.5
Fe_2O_3	0.6 - 3.3	MgO	
SiO_2	2.0 - 9.5	K_2O	0.0 - 0.5
TiO_2	1.5 - 3.5	Na_2O	

Only those of the highest alumina levels are suitable for alumina bricks, but others find use for aluminous qualities.

Bauxite is an ore body produced by tropical monsoomal weathering conditions of parent rocks of the basalt or rhyolite type. They are calcined before being manufactured into shapes to avoid excess shrinkage and frequently mixed with small amounts of highly refractory clays to assist in forming and subsequent processing. Bricks and shapes need to be fired to high temperatures, circa 1600°C to produce hard, dense masses, but such products make excellent refractories able not only to withstand high temperatures but also slags, dust and a high degree of thermal shock. For these reasons they are commonly employed in the roofs of electric arc furnaces for steel melting.

Aluminous Refractories.

Although the terminology of this class of refractories is not internationally standardised, for many reasons it is convenient to classify alumimo-silicates with between 45 - 88% Al_2O_3 by weight as aluminous. As will be shown in the next section, a true fireclay cannot exceed 45% Al_2O_3 by weight on a calcined basis so that a higher alumina level implies the presence of rich alumina-bearing minerals or components.

There are three important but very different categories of refractories in the aluminous range, i) those termed alumina-enriched fireclays, ii) those based on the alumimo-silicate minerals kyanite, sillimanite and andalusite, iii) synthetic mixtures based on mullite.

i) Alumina-enriched fireclays. Some naturally occurring fireclays contain proportions of the hydroxides of alumina; some bauxites contain clay as impurity; in addition some refractories are manufactured from a synthetic mixture of a good fireclay or china clay and bauxite. The results are a high alumina/silica ratio and hence a good refractoriness value, although the improvements in other properties such as refractoriness-under-load and the ability to withstand molten slags and metals are not so marked. Compositions throughout the aluminous range are manufactured and are produced simply by adjusting the ratio of fireclay and bauxite or calcined bauxite.

In order to produce a hard, dense aluminous refractory from clay/bauxite compositions a high kiln-firing temperature is required but this results in a large shrinkage and a tendency to distortion. The product is usually rich in a glassy phase which is not always acceptable. However, in terms of straight heat resistance at temperatures up to 1800°C these materials are excellent and economical.

ii) Kyanite-based refractories. An important group of high alumina refractories is made from the three alumino-silicate minerals, kyanite, andalusite and sillimanite, all of which have the composition $Al_2O_3.SiO_2$.

Kyanite occurs the most frequently; large deposits may be found usually in massive rock form, metamorphosed by heat and pressure. Pure crystals of up to 3 in. in length may be present in an interlocking aggregate contaminated with small amounts of pyrophyllite and quartz. Kyanite is also present in schistose materials, where kaolinite has been hydrothermally altered. Most deposits of kyanite are insufficiently pure in their natural state and have to be purified by froth flotation methods.

Andalusite is less common, but deposits are worked for refractory purposes. The principal form is a massive, metamorphosed rock, but fairly pure samples are occasionally found which have been weathered from such rocks and deposited elsewhere as silt or sand.

Sillimanite is also uncommon but unlike kyanite, sillimanite undergoes scarcely any change in volume on calcining and the raw material can be used directly in furnace settings without any pre-firing. Sillimanite results from the metamorphism of pure clays and contains only minor amounts of quartz, biotite and cordierite, although there may be small amounts of excess alumina as corundum (α-Al_2O_3). The chemical composition of typical samples of the three minerals is shown in Table 3, along with some characteristic properties.

Topaz, $Al_2SiO_4(F,OH)_2$, is converted into mullite when heated to 1300°C and so can be used in the manufacture of high-alumina refractories.

Table 3. Composition and Properties of some Alumino-silicates.

	Kyanite (S. Africa)	Andalusite (California)	Sillimanite (Assam)
	per cent	per cent	per cent
SiO_2	35.5	33.9	35.7
Al_2O_3	61.2	57.6	62.3
Fe_2O_3	0.9	1.6	1.7
TiO_2	1.1	1.5	0.2
CaO	0.1	1.3	Trace
MgO	0.2	0.8	0.1
Na_2O	0.1	0.6	Trace
K_2O	0.1		
Loss on ignition	1.2	3.5	0.7
Refractive Indices	1.713-1.728	1.623-1.645	1.657-1.684
Specific Gravity	3.6	3.1-3.2	3.08
Hardness	7.5	7.5	7.5
Volume change on calcining	+20%	+4%	+0.5%

The three minerals kyanite, sillimanite and andalusite on heating to high temperatures all undergo structural changes to the minerals mullite and cristobalite

$$3(Al_2O_3.SiO_2) \longrightarrow \underset{\text{mullite}}{3Al_2O_3.2SiO_2} + \underset{\text{cristobalite}}{SiO_2}$$

The calcined form has a density of 3.03 whereas the original minerals are higher - kyanite very much more so (see Table 3). Consequently in the transformation to mullite a large volume increase occurs which would disrupt any brick or shape in which the mineral were present.

It is usual therefore to precalcine the original minerals to about 1600°C prior to use in refractory compositions. Nevertheless, such bodies have excellent properties because they are so rich in inter-locking crystals of mullite. They will withstand high stress loading almost up to their softening point.

A body composed of calcined kyanite will contain about 70% mullite whereas a mixture of clay and bauxite is unlikely to produce more than 40% of the mineral even after prolonged firing.

iii) Synthetic Mullite. A high refractoriness coupled with the tendency of the mineral to form a hard, dense mass of needle-shaped crystals results in mullite being an excellent component of refractory compositions. It tends to form in many alumino-silicate compositions on firing but it does not develop in large, tough crystals unless a mixture of the ideal composition is raised almost to the melting point. If a low impurity china clay and a high quality alumina are intimately milled together in the correct proportions to produce mullite $3Al_2O_3.2SiO_2$ and then calcined in the range 1750-1800°C a high percentage of crystals formsand an excellent component for refractories is produced. The product can be crushed and used as grog in either conventional refractories or in castable and mouldable compositions.

Refractory Clays.

Although clays are one of the most abundant mineral forms of the earth's surface, those which are refractory and capable of withstanding the conditions in high temperature industrial plants are relatively few. Refractory clays, however, represent the most important single class of raw materials for high temperature applications as far as tonnage is concerned; they range in composition from 20-44% Al_2O_3 on a calcined basis.

All clays are of secondary geological origin; that is, they are the breakdown products of primary igneous masses. Usually their formation is through the agency of simple weathering processes, but occasionally hydrothermal mechanisms are implicit. Although many complex reactions are involved, the main features are:

a) A physical breakdown of primary rock and a consequent reduction in particle size.

b) A chemical attack in which new mineral forms develop. Many of the new species are termed clay minerals.

The secondary minerals along with those which are relatively unaffected chemically by the breakdown processes may be transported by natural agencies, ultimately to be deposited when favourable conditions exist.

There are two major classifications of refractory clays, namely residual - where the material is found in the location in which it is formed; these include lateritic-type clays, and, sedimentary - when the clay has been transported in some way and deposited elsewhere.

Mineralogical Composition. Although clays contain many minerals often of considerable chemical complexity, those which are truly refractory are mostly of simple type. Three mineral species generally predominate and the relative contents of these determine most of the essential properties of refractory clay materials.

1. Kaolin-type clay minerals, with a chemical composition corresponding closely to $Al_2O_3.2SiO_2.2H_2O$ or a structural formula of $Al(SiO_5)(OH)_4$. Such materials confer both a refractory character and plasticity to clays in which they are present, but when they are heated they usually show high shrinkage due to their high water loss. When in a pure state they are not easy to fire and shapes made from them shrink and distort excessively.
2. Micaceous minerals and other alkali-bearing minerals which behave as fluxes or liquid-forming components in clays.
3. Silica minerals, principally quartz, are of common occurrence in clays, and their presence increases the $SiO_2 : Al_2O_3$ ratio which thereby reduces the ultimate refractoriness as shown by Figure II.

Free silica minerals in clays reduce drying and firing shrinkage and in many other ways are of benefit in processing operations, but excessive amounts of quartz can cause problems of thermal shock in refractory settings.

Accessory minerals, for the most part, are detrimental to the refractory qualities of clays and hence they must not be present in substantial amounts. Iron-bearing minerals and those containing alkaline earth elements behave as colouring agents and fluxes, although not usually to such a serious extent as the alkalies. Carbonaceous matter may be difficult to burn out and causes black-hearts or bloating in bricks. Titanium-bearing minerals in clay behave in a similar fashion to free silica.

In most refractory clays, the accessory minerals rarely exceed 10 per cent of the total weight and frequently the combined content of clay minerals, micas and free silica make up more than 95 per cent.

The refractory nature of clays is intimately related to the alumina/silica ratio and to the alkali content; hence the relative proportions of clay mineral, free silica and micas are of the greatest significance. Table 4 lists several typical fireclays, their calculated mineralogical composition and the properties which result.

TABLE 4

Properties and Composition of Typical Alumino-Silicate Fireclays for Refractory Purposes.

	Semi-silica		Siliceous		Low duty		Medium duty		High duty	
Chemical Comp.	a	b	a	b	a	b	a	b	a	b
SiO_2	86.3	77.0	72.6	61.4	59.6	57.1	43.4	43.6	45.0	46.7
Al_2O_3	9.1	14.2	18.2	24.9	24.5	28.4	34.6	36.7	38.0	37.9
TiO_2	0.4	1.3	0.8	1.0	2.5	1.3	1.4	2.4	0.8	0.1
Fe_2O_3	0.4	1.4	2.1	1.8	1.1	1.7	3.6	1.8	0.4	0.7
CaO	0.1	0.1	0.3	0.5	0.8	0.2	0.8	0.7	0.1	0.3
MgO	0.1	0.2	0.2	0.3	1.0	0.3	0.7	0.5	0.2	0.2
K_2O	0.2	1.5	0.8	2.9	1.9	1.1	2.3	1.1	0.2	0.6
Na_2O	0.0	0.6	0.2	0.9	0.3	0.2	0.7	0.4	0.1	0.2
Loss on ignition	3.2	3.6	5.6	5.9	8.2	9.7	12.2	12.4	14.4	13.4
Mineralogical Comp.										
Kaolin-mineral	23	20	38	32	43	61	62	80	93	89
Mica	2	18	9	32	19	11	26	13	3	7
Free silica	76	59	51	32	31	24	5	1	0	2
Others	1	3	2	4	7	4	7	7	4	2
Fired Properties.										
Firing Temp. °C	1400	1250	1350	1200	1250	1350	1320	1450	1550	1500
Volume Contraction	0.1	0.2	3.2	6.3	8.3	11.6	12.0	16.2	22.0	15.2
Bulk density	2.1	1.9	2.0	1.9	2.0	2.1	2.1	2.2	2.4	2.2
Strength (lb/in^2)	3000	2000	2500	1500	1800	3000	3500	4500	5000	3000
Porosity (app) %	16	24	21	24	23	20	22	19	14	20
Refractoriness (P.C.E.)	32	28	29	29	29	30	32	33	35	34
Refractoriness-under-load										
Initial yield	1450	1370	1400	1300	1320	1370	1380	1400	1520	1420
5% subsidence	1500	1430	1470	1340	1370	1450	1440	1500	1620	1500
10% subsidence	1570	1490	1530	1370	1450	1530	1500	1590	1700	1620
Reheat Test										
1350°C	+0.1	+0.1	+0.2	-0.7	-0.4	-0.3	-1.0	-0.2	0.0	-0.1
1410°C	+0.2	+0.3	+0.2	-1.6	-1.5	-1.2	-0.9	-0.5	0.0	-0.3
1450°C	+0.8	-1.2	-1.0	-2.8	-	-	+1.8	-1.1	-0.4	-0.7
1500°C	-1.0	-	-	-	-	-	bloat	-2.2	-0.6	-1.0

The particle or crystallite size of the minerals which are present in refractory clays can modify the predicted properties often to a considerable extent. Larger-particled systems react more slowly than those of similar composition but of finer crystallite size.

When refractory clays are heated to high temperatures they firstly decompose and then two main important reactions occur, i) crystallisation within the alumino-silicates involving the formation of mullite and cristobalite, and ii) liquid formation which cools to a glassy matrix.

These two phenomena, namely crystallisation and glass formation, determine the whole character and property of a clay-based refractory. A low flux (or alkali) content implies minimal liquid formation and crystallisation reactions would predominate. For these to proceed to a state approaching equilibrium or completion, the firing temperature would have to be high but the product would be strong even at high temperatures and under pressure because failure could occur only by rupturing the crystals themselves.

On the other hand, if the flux content is high, the liquid which forms permeates the mass and on cooling the resulting glass binds the shape together. A strong, dense refractory may thus be produced after only moderate firing conditions but, as this product is reheated, the glass progressively softens and the material is not durable and flows under pressure at fairly low temperatures. In other words, it would have poor refractoriness-under-load properties. These factors are clearly shown in Table 4.

Types of Refractory Clays. For a clay to be truly refractory, natural processes of formation must have ensured that minerals containing iron, alkali and alkaline earth elements, and the various forms of free silica are all at minimal levels. Such materials are not of common occurrence and they form only a relatively small percentage of the vast tonnage of other clays found on the earth's surface. However, many countries have suitable varieties although the geological origins may not always be the same.

China clays are generally regarded as being the result of the hydrothermal breakdown of felspars in granites. The clays may be found as in situ residual formations or as sedimentary formations close by the original source. Some good kaolins, however, are undoubtedly the products of laterisation of an otherwise impure and non-refractory clay.

The essential mineral component of china clays is kaolinite; some sedimentary formations contain more than 90% of this mineral; residual deposits can often be readily beneficiated to yield an equally good or better product.

As refractory materials, china clays are generally excellent but they are loose, unconsolidated clays, hence they are difficult to process because of their large shrinkage. Some pre-calcination is usually an essential requirement before refractory shapes can be manufactured from china clays.

Good china clays are rare and valued for other purposes so that their use - except in impure forms - for refractory purposes is limited. The best varieties contain 40-44% alumina on a calcined basis.

Ball clays are not unlike china clays in that they are mostly derived directly from an igneous formation in the near vicinity, but they are invariably sedimentary in origin and contain more impurities than china clays.

The particle size of ball clays is generally very small so that they are plastic and strong. They are useful bonding components for refractories in which a high content of pre-calcined material (grog) is to be incorporated.

Fireclays are the most common type of clay used for refractory purposes. The term was originally a general one used to describe all clays which will resist high temperatures, but nowadays, many ceramists regard fireclays as the seat-earths of coal seams, although not all of these are refractory.

Coal Measure fireclays of many qualities are known; the examples quoted in Table 4 indicate a typical range. In textural characteristics there may also be considerable variations from hard, flint-like materials through shales to sticky plastic forms.

Flint clays are materials of an extremely hard, dense texture. They are rich in kaolin clay minerals and contain only minimal amounts of impurities deleterious to refractory qualities, but they are consolidated to such an extent that even fine grinding will not develop any significant plasticity.

The high bulk density of flint clays makes them especially valuable as components of refractory shapes. They undergo hardly any volume change on drying or firing, but because they are so lacking in plasticity they must be used either in conjunction with a sticky clay or as a type of grog. The essential differences in properties of various clays are shown in Table 5 where in every case a kaolin mineral was the predominant species.

Table 5. Physical Properties of Some Refractory Clays in Natural States.

	China Clay (Georgia)	Ball Clay (Dorset)	Fireclay (Scotland)	Flint Clay (S.Africa)
Bulk Density	2.04	1.98	2.39	2.58
Water Content %	18.4	25.2	6.2	1.2
Drying Shrinkage (volume %)	15.6	22.1	3.3	0.2
+Firing Shrinkage (volume %)	21.2	18.4	10.4	3.4

+Firing shrinkage based on a product with a water absorption of less than 2%.

Other refractory clays are known which cannot be included in any of the categories listed above. Although most clays of recent geological origin and those which occur as surface deposits are too rich in low melting impurities to be considered as refractories, there are exceptions.

Occasionally, unusual physical conditions during formation, transportation or deposition can result in a clay which is low in iron, alkaline earth and alkali elements, so that reasonably good refractory qualities might occur in any deposit. It is not unusual to find specific levels of clay in a brick-making quarry which are appreciably more refractory than the average for the whole face. Such seams are often exploited on a limited scale to manufacture a refractory quality suitable for lining the brick-making kilns.

The important advantages of refractory clays are that they are easy to mine, they require little complex or expensive processing, they can be manufactured either into simple brick form or into complex shapes with low cost, uncomplicated equipment and they can be fired to good dense refractories without the need for very high temperatures.

Despite these advantages, the fireclay refractory is declining seriously in modern high temperature practice. This is due to the changes in steel-making practice as a result of basic oxygen processes and to a lesser extent to the introduction of castable and mouldable compositions which require less labour for installation.

Nevertheless, refractory clays are important refractory raw materials indigenous to many countries and suitable for numerous applications in the high temperature industries, including steel, particularly when highly automated units using basic oxygen are not involved.

<u>Siliceous Refractory Clays</u>. Although the phase diagrams (Figures I and II) suggest that alumino-silicates with a silica content in the range 80-95% are the lowest in refractory value, materials of this composition are excellent for certain applications. The raw materials for such refractories are clays, rich in free silica (quartz) but with the minimum of other impurities.

When such compositions are heated to high temperature, the liquid which forms is highly siliceous and tends to be very viscous so the material does not yield or slump readily. In addition the quartz tends to convert to other crystalline forms of silica, such as cristobalite and tridymite and, in so doing, it expands and mitigates the contraction tendency accompanying the formation of liquid.

Siliceous and semi-silica refractories are valued therefore for their volume stability. They shrink only slightly on firing and preserve their size and shape in furnace installations for considerable periods of time provided that excessive temperatures (+ 1450°C) are avoided. Steel billet soaking pits are an excellent application for siliceous fireclay products.

Pyrophyllite, $Al_2O_3.4SiO_2.H_2O$, is an important raw material used for refractories, electro-ceramic bodies and in the manufacture of tiles. The mineral is thought to have been formed by the hydrothermal replacement of acidic volcanic glasses. It occurs in massive flake-like form, not unlike mica, but softer and more brittle. Pyrophyllite is valued for its low shrinkage on firing - it loses its water of constitution at about 600°C and forms mullite and cristobalite above 1100°C. An analysis of a typical sample shows SiO_2 77.4 per cent; Al_2O_3 16.5 per cent; Fe_2O_3 0.5 per cent; MgO 0.05 per cent; CaO 0.41 per cent; Na_2O 0.22 per cent; K_2O 1.26 per cent; and loss on ignition 2.87 per cent. Siliceous bricks of excellent volume stability up to 1500°C can be made from it.

Silica Bricks.

Silica bricks are usually made from rock containing at least 97 per cent of silica, but the following range of composition is accepted:

Silica	95 - 99%	Titania	0.2 - 2.5%
Alumina	0.1 - 2.8	Lime	0.2 - 2.4
Iron oxide	0.3 - 1.3	Soda & Potash	0.2 - 1.5

Alumina is an undesirable impurity and for each 0.1% Al_2O_3 in the composition, the maximum usable temperature of the refractory is decreased by 10°C.

The raw material for silica refractories can range from high density consolidated quartzitic rock to loose uncompacted silica sand or pebbles. The material may be well-crystalline, cryptocrystalline or amorphous.

Neither quartz nor amorphous silica is stable at high temperature and on firing they convert to other crystalline forms of silica, namely cristobalite or tridymite. If the kiln firing is incomplete further conversion is liable to occur in use and this change is accompanied by a large volume expansion. Silica bricks need to be fired to a high temperature (about 1450°C) and maintained there for some considerable time during manufacture. Quartzites with some amorphous component are best and the addition of lime or iron oxide as catalysts is of assistance.

Silica refractories are good, cheap products ideally suited to many high temperature operations. The best are capable of withstanding 1700°C under stress conditions. They are unable to withstand serious alkali slag attack and they are liable to thermal shock if allowed to cool between furnace reheats. However, countries without indigenous basic refractory materials and with a small steel industry not based on oxygen furnaces will find many economical outlets for silica. Iron melting cupolas, for example, can be lined with hewn ganister blocks which do not require firing before use

Silica sand is widely used in ramming compositions and in foundry operations (see Chapter IV).

In modern steel plant practice, the fired silica brick has been largely superseded by other types of refractory so that its tonnage usage nowadays is drastically reduced.

Suggestions for further reading:

R. W. Grimshaw, "Chemistry & Physics of Clays and other Ceramic Materials", Ernest Benn Ltd., 1971.

W. E. Worrall, "Raw Materials", Inst. of Ceramics Textbook Series No.1, Maclaren & Sons Ltd., London, 1965.

III. BASIC REFRACTORIES.

Alumino-silicate refractories, particularly those which are clay-based and contain more than 55% SiO_2, cannot withstand basic slags of the composition and temperature encountered in the modern steel industry. The temperature at which certain steels are refined can be as high as 1800°C; viscous lime slags, often with fluorspar additions, are employed to ensure that acid components are effectively removed from the metal; the air or oxygen blast is at elevated temperatures and it is frequently charged with high velocity dusts rich in iron oxide. These conditions can be endured only by refractories which are themselves basic in character.

Reference to Table 1 (page 2) shows that the alkaline earth oxides are of high refractoriness and are chemically basic. But of the five oxides in Group II of the Periodic system, beryllia is rare and toxic, lime, strontia and baria cannot be heat-stabilised adequately. The only oxide which can form satisfactory refractory materials is <u>magnesia</u>. Modern technology has now partially overcome some of the serious disadvantages of the lime component in calcined dolomite, so that this mineral can also form a useful range of refractories.

No other mineral or chemical form can be manufactured into successful basic refractories to be used on a large scale, but chrome ore has proved to be a useful additive to magnesia compositions. Silicates of magnesia, provided that the molar ratio of $MgO:SiO_2$ is not less than 2:1, also have limited application as basic refractories.

<u>Magnesia Refractories</u>.

Some common forms of magnesia-containing minerals will decompose on calcination to give the oxide. Although when formed in the 500–700°C temperature region, magnesia is caustic and readily hydrates, it can be converted to a stable form known as <u>periclase</u> by heating it at temperatures in excess of 1500°C.

The principal magnesium minerals which are used in the manufacture of magnesia refractories are:

Magnesium carbonate or *magnesite* ($MgCO_3$) which occurs in two main varieties, a) a spathic or coarsely crystalline form, and, b) a dense crypto-crystalline type which is usually purer than the former. These are precipitation minerals formed naturally from sea water; impurities of silica, lime, iron oxide and some clay are liable to be present and occasionally graphite derived from decaying vegetation. Subsequent consolidation by overlying strata and by land movements gives rise to a hard dense body.

Magnesium hydroxide or brucite $Mg(OH)_2$ which is much less common than the carbonate and is rarely as pure.

Sea water magnesia produced by the chemical treatment of sea water is now the most important raw material for magnesia refractories. The 0.7% magnesium salts in solution - which is the normal concentration in sea water - can be recovered virtually quantitatively as the insoluble hydroxide simply by making the water alkaline with slaked calcined limestone thus:

$$\begin{array}{ccccccc} MgCl_2 & & & & & & CaCl_2 \\ \text{or} & + & Ca(OH)_2 & \longrightarrow & Mg(OH)_2 & + & \text{or} \\ MgSO_4 & & & & & & CaSO_4 \\ \text{(in solution)} & & & & \text{(insoluble)} & & \text{(soluble)} \\ \text{(in sea water)} & & & & & & \end{array}$$

The precipitated magnesium hydroxide can be filtered, washed and calcined to about 1500°C to produce stable periclase.

The type and amount of impurities in the periclase are all-important, because some of these combine together and with magnesia to form complexes of low melting point which seriously reduce the refractory qualities. However, by carefully controlling the conditions of precipitation it is possible to reduce the impurities to a very low level and produce a superior quality essential for the stringent conditions of an oxygen vessel or similar application.

When magnesia is fired in the form of refractory shapes or to make grog, any impurities react both with the magnesia and within themselves often to produce complexes of low melting point.

Alumina is a serious impurity and in best quality refractories it should not exceed 0.5%. Iron oxide is less harmful but it should not be present in amounts greater than 1.5%.

The ratio of $CaO:SiO_2$ is important and must be controlled at about 2.5:1 molar; the silica content should be maintained below 1.0% by weight. If the boric oxide content of magnesia is allowed to exceed 0.02% a marked reduction in high temperature strength results.

High quality magnesias are now manufactured to meet the stringent conditions imposed in oxygen-blown vessels in the steel industry. These conform to the above chemical specifications but care has to be taken to ensure high density and strength.

The precipitated $Mg(OH)_2$ is firstly lightly calcined to about 900°C to remove all combined water and to produce an "active" oxide. This is then pelletised at high pressure and finally calcined at about 1750°C. This produces a grain of high density and low porosity which is then crushed and graded to form the raw material from which bricks and shapes are prepared. These are usually pressed at about 10 tons/sq.in. and fired to at least 1750°C or chemically bonded.

Not all magnesia refractories are manufactured to these stringent conditions. Chrome/magnesite refractories, gunning and fettling compositions, forsterite synthesis and other applications can be manufactured from lower quality magnesia typical of natural minerals or the more usual sea water products. Table 6 indicates the range of composition accepted for magnesia products of general application.

Table 6. Analyses of Typical Calcined Magnesites.

	Spathic	Cryptocrystalline	Sea Water
MgO	80 - 92%	92 - 98%	85 - 95%
Al_2O_3	0 - 4	0 - 2	0 - 6
Fe_2O_3	2 - 9	0 - 1	2 - 6
CaO	1 - 6	1 - 5	2 - 5
SiO_2	1 - 10	0 - 4	2 - 4

The impurities, although they form low melting point liquids, do help in consolidating and densifying the bricks and imparting hardness. However, it must be emphasised that inferior quality basic refractories give markedly poorer performancesin steel plants, cement kilns, etc., so much so that their benefits in some applications over the much cheaper and easier to manufacture indigenous fireclay and silica refractories can at best be marginal.

Dolomite Refractories.

Dolomite or magnesian limestone is a magnesio-calcium carbonate, the chemical formula of which can be represented ideally as $MgCa(CO_3)_2$. It is formed either by co-precipitation of the carbonates of calcium and magnesium from sea water or through the percolation of solutions rich in magnesium salts through limestone rock, with subsequent replacement of calcium by magnesium.

On calcination, dolomite decomposes into an intimate mixture of lime and magnesia; after intense heating, the magnesia will form stable periclase whereas the lime retains its tendency to rehydrate no matter how hard the firing treatment. Although this is a serious disadvantage, calcined dolomite is such a good basic refractory and the mineral form is so much more prolific and cheaper than magnesite, that dolomite is used extensively particularly in modern steel plant practice.

As is the case with magnesia, unavoidable impurities associated with dolomite reduce the refractory quality. The main ones are alumina, silica, and iron oxide which tend to form liquids at moderate temperature and so reduce the ability of the refractory to withstand stresses at high temperatures.

Dolomites for refractory purposes have to be selected with care to minimise the deleterious effect of impurities. The range of composition of acceptable dolomites is as follows, but the superior qualities are derived from those materials with the minimum impurity levels and the highest magnesia:

CaO	28 - 34%	SiO_2	0.2 - 1.0%
MgO	16 - 22	FeO	0.1 - 0.4
Al_2O_3	0.1 - 0.7	Fe_2O_3	0.2 - 1.5

Loss on ignition 45.0 - 47.5%

The rehydration tendency of calcined dolomite can be reduced in one of three ways:

i) Chemically, by converting the lime to tricalcium silicate by the addition of talc or serpentine and then hard firing. Chemically stabilised dolomite bricks have their merits but they are difficult to manufacture and their high temperature properties are not good.

ii) Pitch or tar-bonded. In effect the unstable lime component in fired dolomites is shielded from atmospheric rehydration by a water-proof coating. The dolomite is calcined and crushed to a suitable size grading. Pitch or tar is added hot and blended with the composite which is then pressed into bricks or complex shapes of high density.

This technique is satisfactory in that the bricks are well able to resist hydration during normal storage prior to being installed in the furnace. Once they have been fired, however, the protective layer is destroyed and if the installation is allowed to cool, rehydration can then occur with potential disruption of the setting.

iii) High density pelletisation. A calcined dolomite grain is prepared by a two-stage firing process. Initially a low temperature burn to about 900°C produces a mixture of active oxides which are then pelletised. The grains are dead-burned or sintered at a temperature of about 1800°C so that the product has virtually no porosity. The surface area of lime thus available for rehydration is dramatically reduced and for most purposes the grains may be regarded as stable. In addition the pellets are exceptionally strong and hard so that when they are compounded into block form - usually with pitch binder - the product is able to withstand severe erosion and corrosive slags.

This method of stabilisation is now in general use and it undoubtedly produces a vastly superior dolomite refractory of great value as side walls in electric arc furnaces, in the burning zones of cement-kilns and as linings for oxygen vessels in steel refining.

Dolomite refractories enriched with magnesia to raise the MgO level are also successful; the refractory qualities are improved, particularly the resistance to slags containing iron oxide and the rehydration tendency is markedly reduced. A total MgO content between 55-70% gives the best results.

Chrome-containing Refractories.

It is frequently assumed that because chrome ore is a common constituent of basic refractories, chromic oxide is itself alkaline in character. This is incorrect; chromic oxide is, in fact, acidic, but its value in refractories is associated with its capacity to play a major role in the formation of the spinel group of minerals. Many of these are highly refractory and form hard dense crystals, a vital prerequisite for refractories which are required to withstand high stresses and corrosive slags.

The raw material from which chrome-based refractories are manufactured is chrome ore, the usual geological occurrence of which is as segregations in ultra-basic rocks.

The essential mineral form of chrome ore is spinel which has the general form $R^{2+}O.R^{3+}{}_2O_3$,
where R^{2+} is a divalent cation such as Mg,Zn,Fe^{2+}
and R^{3+} is a trivalent cation such as Al,Cr,Fe^{3+}.
Chromite $FeO.Cr_2O_3$ or $FeCr_2O_4$ is the closest representation of the spinel form in most chrome ores but there is considerable substitution of magnesium for ferrous iron and aluminium and ferric iron for chromium.

Good quality chrome ores are not of common occurrence but there are several interesting areas of potential development particularly in Africa and S. E. Asia.

It is not easy to specify compositional ranges for chrome ore for refractory purposes. It is essential that when the mineral is fired, the maximum amount of spinel should develop with the minimum of low melting point accessory minerals. Lime as CaO should be low in content and ideally the molecular ratio of $CaO:SiO_2$ should be in the range 0.5-1.0:1. If there is an excess of lime over silica there is a tendency for calcium ferrite, aluminate and chromite to form, which all melt at low temperature. A slight excess of silica over lime is less harmful because this will combine with magnesia to form the high melting mineral, forsterite. Exceptionally high ferrous oxide (FeO) contents - in the range 25-30% - present problems of large volume expansion on firing although these can be largely mitigated by careful control of firing. Acceptable chrome ores from various world localities vary considerably in the content of their major oxides as the following list indicates:

Cr_2O_3	33 - 55%	MgO	10 - 20%
Al_2O_3	13 - 30	CaO	0 - 1
Fe_2O_3	0 - 5	SiO_2	2 - 7
FeO	12 - 30		

Chrome ores are only rarely used nowadays as a refractory in their own right but when blended with dead-burned magnesia they form one of the most important classes of basic refractories. The undesirable impurities alumina and iron oxide tend to enter a refractory spinel phase, excess silica combines with magnesia to form refractory forsterite leaving only the minimum of low melting phases which reduce the refractoriness-under-load and increase the tendency to slag attack. The magnesia used as additive must be low in lime.

Both chrome-magnesia and magnesia-chrome refractories are manufactured in which the first-named component is the major constituent; 70/30 compositions are commonly employed. Bricks are manufactured either by chemically-bonding dead-burned graded clinker or by directly firing compositions in the range 1700-1800°C to develop adequate ceramic bond.

Magnesia/chrome compositions have wide applications in the steel industries and elsewhere where high temperatures under basic corrosive conditions are likely to apply. Electric arc [illegible], open hearth furnace walls and roofs, cement kiln burning zones, glass tank regenerator blocks are but a few examples of applications for this type of refractory. Qualities vary depending on the purity of material, the methods used in forming (should be hard pressing), the density of the calcined grain and the intensity of the final burning. The best grades are excellent refractories; inferior grades can still be very acceptable, more so than inferior grades of magnesites and dolomites.

Forsterite Refractories.

Refractories consisting essentially of forsterite $2MgO.SiO_2$ have a limited application as basic refractories. Either a natural olivine or dunite rich in magnesia or a compounded mixture of talc, serpentine or steatite sometimes with magnesia additions are used as raw materials.

Ideally forsterite consists of 57.1% MgO and 42.9% SiO_2 on a weight basi

Some ferrous iron can enter the lattice but other impurities such as lime and alumina form low melting point complexes. Forsterite is not as good as a refractory as magnesia and dolomite compositions but where raw materials are available cheaply it can be a worthwhile product. It is used extensively as a component of ramming mixes in some small steel ladles.

Suggestions for further reading:

J. White, Refractory Materials Volume 5 - 1, Academic Press : New York and London, 1970, p.77 ff.

J. Laming ibid p.143

D. R. F. Spencer, Basic Refractory Raw Materials, Trans. Brit. Ceram. Soc., 71 (5) 123, 1972.

J. Halm, J. Brit. Ceram. Soc., 7, 42, 1970.

IV. CASTABLES, MOULDABLES AND CHEMI-BONDED COMPOSITIONS.

Although products known generally as castables and mouldables are of comparatively recent introduction into the refractories industry, their present day usage and applications are extensive.

The compositions are composed mainly of pre-fired refractory material or "grog"; in castables, a proportion of cementing agent, either hydraulic or chemical, is added so that the product air-sets and is then load-bearing. In mouldables, plasticity is conferred by clays or organic materials which give a small degree of air-set, but ultimate high strength develops through a ceramic bond induced only after high temperature operation. In chemical bonding a reagent is added to the grog mixture which develops a crystalline phase by chemical combination.

Castable and mouldable materials can be applied in situ by a variety of techniques to form a monolithic unit capable of complex design. Chemi-bonded products can be used in the same way, but they are also manufactured into bricks and standard shapes which set hard and do not need kiln firing prior to their installation in furnace settings.

The basic functions of these compositions are that, through the lubricating medium of water they can be easily installed in a furnace or moulded to shape and subsequently they will develop strength by virtue of heating in situ or by hydraulic or by chemical reaction without losing shape or contracting in any way.

Castables contain a refractory cement or a chemical bond as an essential ingredient. When mixed with water and the composite cast or gunned into place, the whole structure sets hard.

Mouldables are plastic compositions usually made so by the inclusion of a refractory clay. They can be rammed or pressed into place and although they do not develop high dry strengths they have minimum shrinkage on drying and firing and they develop a ceramic bond at high temperature.

Raw Material Specifications.

1. **Grogs.** Because they usually make up 60-90% of the total composition, the grogs or pre-calcined constituents largely dictate the nature of the product in which they are present. The range of suitable materials is wide and only a few common ones are shown in Table 7.

Other grogs which deserve special mention are those used in insulating castables; these include calcined diatomaceous earth, exfoliated vermiculite, bloated fireclay and bubble alumina.

In preparing grogs for use in castables and mouldables, their physical properties are at least as important as their chemical composition. In order to ensure high strength and low shrinkage, the grog must be dense and hard. The practice of using scrap refractory bricks as grogs cannot be recommended. The inherent high porosity and weaknesses of such materials should preclude their use and only grogs prepared by calcining lump virgin minerals are truly acceptable. As Table 7 shows, high bulk densities and the accompanying high degree of vitrification should always be sought.

2. **Cements and Bonds.** a) The cementing agents used in castables to give high dry strengths depend on the temperature at which it is to be used. Ciment fondu and high alumina compositions are mostly employed but there are other proprietary cements. These form hydrates in the presence of water; bonding is the result of interlocking crystalline growth throughout the mass. The dry strength which develops in a castable composition depends on the amount of cementing agent present, but high contents of cement reduce refractoriness and increase cost. Most commercial mixtures are based on either a 1 : 6 or a 1 : 4 cement : grog ratio.

b) The two best known examples of chemical bonds are phosphates (most commonly in association with alumina) and chromates (combined with magnesia). The bonds are frequently added as acids (1-5% by weight) which react slowly with the particles of aggregate in the presence of water. Sodium silicate and aluminium sulphate also are added as chemical bonds, and some oxy-salts are frequently utilised.

Table 7. Some Typical Grogs Used in Castables and Mouldables.

	Fused Alumina	Calcined Bauxites	Synthetic Mullite	Sillimanite	Calcined Flint Clay	High grade calc. fireclay	Low grade calc. fireclay	Abrasion resistant grog	Calcined Dolomite	Sea Water magnesia	Calc. magnesite
SiO_2	0.1	6.2	29.7	35.7	51.2	54.2	55.4	62.5	0.4	2.0	0.8
Al_2O_3	99.5	87.4	66.2	62.3	44.1	42.1	35.2	30.0	2.1	0.3	0.2
Fe_2O_3	0.1	1.6	1.5	1.7	0.8	1.3	2.6	2.0	0.8	0.6	0.2
TiO_2	0.0	3.6	2.0	0.2	3.5	1.4	1.3	1.0	0.4	0.3	0.1
CaO	0.0	0.2	0.2	0.0	0.1	0.2	0.3	0.2	56.2	1.1	3.2
MgO	0.0	0.1	0.0	0.1	0.1	0.3	0.4	0.5	40.0	96.5	95.0
K_2O	0.0	0.2	0.3	0.4	0.3	0.5	1.5	3.2	0.2	0.1	0.2
Na_2O	0.1	0.2	0.2	0.2	0.1	0.1	0.6	0.8	0.1	0.0	0.2
Bulk Density	3.8	3.4	2.8	2.6	2.5	2.4	2.1	2.3	3.0	3.2	3.1
Max. Service Temp. °C	1750	1600	1700	1650	1550	1500	1400	1350	1650	1750	1700

c) In mouldable compositions, where high dry strengths are not required, the bonding agents are very different in character. They are intended to confer just sufficient adhesion for the mass to hold together in the wet and dry states. Plastic clays, up to 20% in amount, are generally preferred, but organic bonds such as cellulose sulphite lye, dextrin, various gums, molasses and starches are also in common use in amounts between 0.5 - 2.0% of the total composition.

3. Special additives. One advantage of castables and mouldables is that they can readily be 'tailor-made' to suit any particular industrial requirement. Occasionally special mineral additives prove advantageous. These include kyanite, valued for its expansile characteristics and graphite, which is remarkably resistant to molten slags and metals.

It is an obvious fact that all the components of a castable must be thoroughly dried before being mixed. It is usual for the manufacturer to despatch the complete mixed dry ingredients in bags for water to be added immediately prior to installation.

Chemically-bonded products may contain the additive premixed in solid form or supplied as a separate solution to be added with the mixing water.

Mouldables are often delivered to the installation point with the requisite amount of water already added. No further mixing would be needed thus greatly reducing the labour required on site. In the best practice, the mouldable is supplied as extruded, de-aired blocks of high density, packed in plastic bags.

Particle Size Distributions.

Most compositions demand that the packing density of the installed material must be at a maximum, otherwise bonding is incomplete and shrinkage in service is likely to occur. The normal rules of good packing must be rigidly observed. A simple but excellent control is to represent the complete grading, as determined on a nest of sieves, as a graph with the percentage of material above a certain size plotted against the particle size (or logarithm of particle size) in microns. From the graph two important parameters can be calculated simply, a) the centre grain size or the size at 50% retention, and, b) the quartile ratio, i.e. the ratio between the micron size at 25% retention against that at 75% retention. For good packing this value should lie between 16 - 22. Provided that the size distribution graph is smooth, this value of quartile ratio will ensure that the mix will have a dense packing but not be too impervious to prevent water release or gaseous escape.

The centre grain size of a mixture must also be selected with care. For normal castables and mouldables a centre grain size of about 350 microns is preferred which implies a maximum size of 4 mesh B.S.S. If the product has to withstand high thermal shock, a coarser grading of about 600 microns centre grain size (maximum grading 3 mesh B.S.S.) is better. When high abrasion or corrosion resistance is required a fine texture is essential with a centre grain size of 200 microns and a maximum size of 6 mesh B.S.S. or less. Gradings, particularly of mouldables, are best determined by wet methods.

When chemical bonding is involved, it is essential that a greater proportion of the grog should be of very fine particle size - less than 200 mesh B.S.S. This is to ensure reaction with the chemical additive.

Applications.

Because installation costs of conventional refractory bricks and shapes have become so high in recent years, castable and mouldable compositions have gained in importance and application, particularly when complex structures have to be constructed. Monolithic installations have the added advantages of being jointless and they can be closely contoured to improve gas and liquid circulation, but the cheapness and speed of construction are the important factors.

Castables and mouldables can be adapted to suit the particular refractory requirements of general application in high temperature practice. Chemi-bonded qualities are necessary for extreme conditions of erosion and corrosion although where high impermeability, corrosion resistance or mechanical abrasion is involved, conventional bricks and shapes frequently give better performance.

Wherever frequent replacements of refractories are envisaged, mouldables offer marked advantages. Runners, ladles, hearths are frequently lined with these products.

Ramming Compositions.

Closely related to mouldables are various compositions used for fettling or ramming purposes. These are usually employed when excessive wear is encountered so that frequent patching or replacement is necessary.

Basic fettling and ramming compositions consisting mainly of tar-bonded magnesia or calcined dolomite are commonly used in steel melting vessels, but sand-based products are being increasingly preferred to conventional firebricks in steel ladles. The requirement is a clean sand, well-graded but fairly fine-grained (centre grain size about 100 microns); a proportion of a plastic refractory clay is also essential but this must be in minimal amounts consistent with good strength. The clay is either a natural component or it is added to the sand during processing. Zircon and olivine in a sandy form are being used on an increasing scale for these purposes.

Jointing compositions and refractory lutes are manufactured from very finely crushed grogs and sands with some clay or organic bond; frequently sodium silicate or some other chemi-bond is also included.

V. SPECIAL REFRACTORIES.

If one takes into account the recent rapid advances in refractory technology in the fields of nuclear energy, aerospace and missiles, gas turbines, energy production and distribution, and other exotic applications, the number and type of new special refractories are legion. This is largely because so many other unusual characteristics have to be combined with a high melting point. It is not within the present context to discuss all the rarer applications, but nevertheless there are several mineral forms, whilst not of common or large scale use, which are sufficiently important to warrant reference here.

Special Refractory Compositions.

Carbon refractories - based on natural or synthetic graphite - are the only products manufactured on a large scale in which the main component is an element. Carbon has the unique property of not being wettsd by molten slags or metals. Its melting point is in excess of 3500°C, but it is liable to oxidation above red heat if oxygen is freely available. However, if this latter problem can be overcome, carbon has many interesting applications.

Graphite - especially very pure varieties - can be prepared by synthetic means from asphalt, pitch or some other organic species, but in recent years much more natural mineral has been used for refractories; it is of metamorphic origin and it can occur either in flakey or amorphous varieties. The former is the purer and is used extensively in crucibles and for some bricks. Amorphous graphite containing +90% C is an important component of ramming mixes to withstand molten metals and slags and also in foundry compositions.

When graphite is used in refractories,its oxidation tendency can be mitigated either by adding clay as a coating or by incorporating a ceramic frit or glass which melts on heating and seals the graphite into an air-tight form.

Carbon bricks of high density and formed in high duty presses into large blocks make up the hearths of many blast furnaces. Graphite is also used in stopper assemblies of ladles, particularly the ends or heads which have to be shaped to precise limits to fit tightly into the nozzle.

Beryllia, BeO, is part of the alkaline earth oxide series; it would be a super-refractory if it were non-toxic and of more common occurrence. Although its melting point is 2570°C it sinters readily to a dense impervious mass at about 1300°C. It is not as brittle as most refractories and has an excellent resistance to thermal shock.

Its main mineral occurrence is beryl, $3BeO.Al_2O_3.6SiO_2$ - a rare mineral associated with felspars. It is used in the manufacture of some crucibles for special melting purposes, gas-turbine blades and rocket nozzles.

Zirconia, ZrO_2, is found as the mineral baddeleyite. It has great potential as a refractory and interest has increased in its use following the discovery that appreciable quantities can be recovered from the tailings of copper processing in S. Africa. When it is manufactured n stabilised form,it has excellent resistance to corrosive dusts of both basic and acidic character.

Zircon, $ZrSiO_4$, is more common in that it is an accessory mineral in the black beach sands worked extensively for ilmenite, rutile and monazite. This mineral is also refractory and it can be manufactured into dense, hard products of excellent shape. It is frequently used in pouring spouts or nozzles in continuous steel casting and in glass-forming processes. The largest tonnage application is as a super-quality sand for small ladles for special steel manufacture.

The product derived directly from the electromagnetic and electrostatic processing of monazite sands is usually sufficiently pure for refractories, but an iron oxide content of less than 1.0% is preferred.

Thoria, ThO_2, can be recovered from the monazite mineral of beach sands and from other sources, but a complex chemical process is involved. It is an excellent refractory, melting at an elevated temperature, but because of its rarity and high cost it is mostly confined to laboratory ware. Other rare earth oxides are also of interest.

Silicon Carbide, SiC, is the only synthesised compound to be used on a large scale as a refractory. It is prepared by fusing a mixture of pure sand and coke in an electric arc at temperatures in excess of 2000°C. The resulting clinker of silicon carbide is hard and refractory, possessing some of the advantageous properties of graphite, but without the problems of softness and severe oxidation tendency.

Silicon carbide refractories are made from the ground and graded clinker from the arc furnace,usually with added binder or chemical bond and then fired to + 1600°C. The refractory is hard, very resistant to slags and metals, with a good thermal shock resistance and a higher electrical conductivity than most other refractories.

Other carbides may be prepared in a similar way but because of their high cost they are not used as commonly in refractory practice as is the silicon derivative. Tungsten, titanium and molybdenum are produced on a limited scale and used mostly for applications other than refractories.

Nitrides, particularly those of silicon and boron, offer exciting possibilities as the refractories of the future. They are synthesised from the appropriate oxide or element which is heated in a nitrogen atmosphere. The properties which these forms possess are unusual and there is considerable potential scope for their development.

Special Forming Methods.

Some refractories may be regarded as special, not necessarily for the materials which they contain, but because of the way in which they are processed and the unusual character of the product.

Insulating Refractories. In the context of heat, an insulating character implies that the body prevents the transmission of heat or that it has a low thermal conductivity. The actual substances of which refractory materials are composed are all appreciably more conductive to heat than air itself except perhaps at very high temperatures, so thermal insulation depends largely on the volume of pores which can be incorporated in the body. However, the size of pores and the way in which they are arranged are also important. Small pores restrict heat transmission by convection and, if they are largely disconnected, the insulation is further improved because the body becomes impervious to hot gas flow.

Some minerals are naturally good insulators:

Diatomite is perhaps the best in that it consists of the siliceous skeletal remains of tiny sea organisms. It can be manufactured into bricks or used as a loose composition. The best grades consist of fairly pure silica and are low in iron oxide so they can be used up to 1200°C hot face temperature. The more usual qualities are less pure, being richer in alkalies and iron oxide, but nevertheless they are excellent insulators up to their sintering point of about 900°C.

Asbestos minerals, particularly chrysotile $3MgO.2SiO_2.2H_2O$, are excellent thermal insulators, but at about 600°C they decompose and tend to lose their fibrous form. Asbestos is a major component of shapes and loose fill for use as "back-up" insulation in kilns and furnaces.

Vermiculite, a complex hydrated magnesium silicate, not unlike biotite mica, exfoliates on heating to form an excellent thermal insulator. It can withstand slightly higher temperatures than diatomite.

Perlite is a type of basalt igneous rock which bloats on heating to about 900°C. The honeycomb structure which results has excellent insulation characteristics. A somewhat similar product can be made from certain shales.

The naturally-occurring mineral forms, whilst possessing excellent insulation properties, are not usually sufficiently refractory to withstand the high temperatures of industry. Porous bodies are therefore manufactured from many refractory compositions by incorporating into the mix some finely-divided combustible material such as paper-pulp, saw-dust, pulverised coal or fine plastic powder. These burn away on firing leaving a porous structure. Porosity can also be induced by developing bubbles of air or gas during forming. Insulating bricks of the whole alumino-silicate range and of basic compositions can be made in these ways. Castable and mouldable insulating compositions are also manufactured.

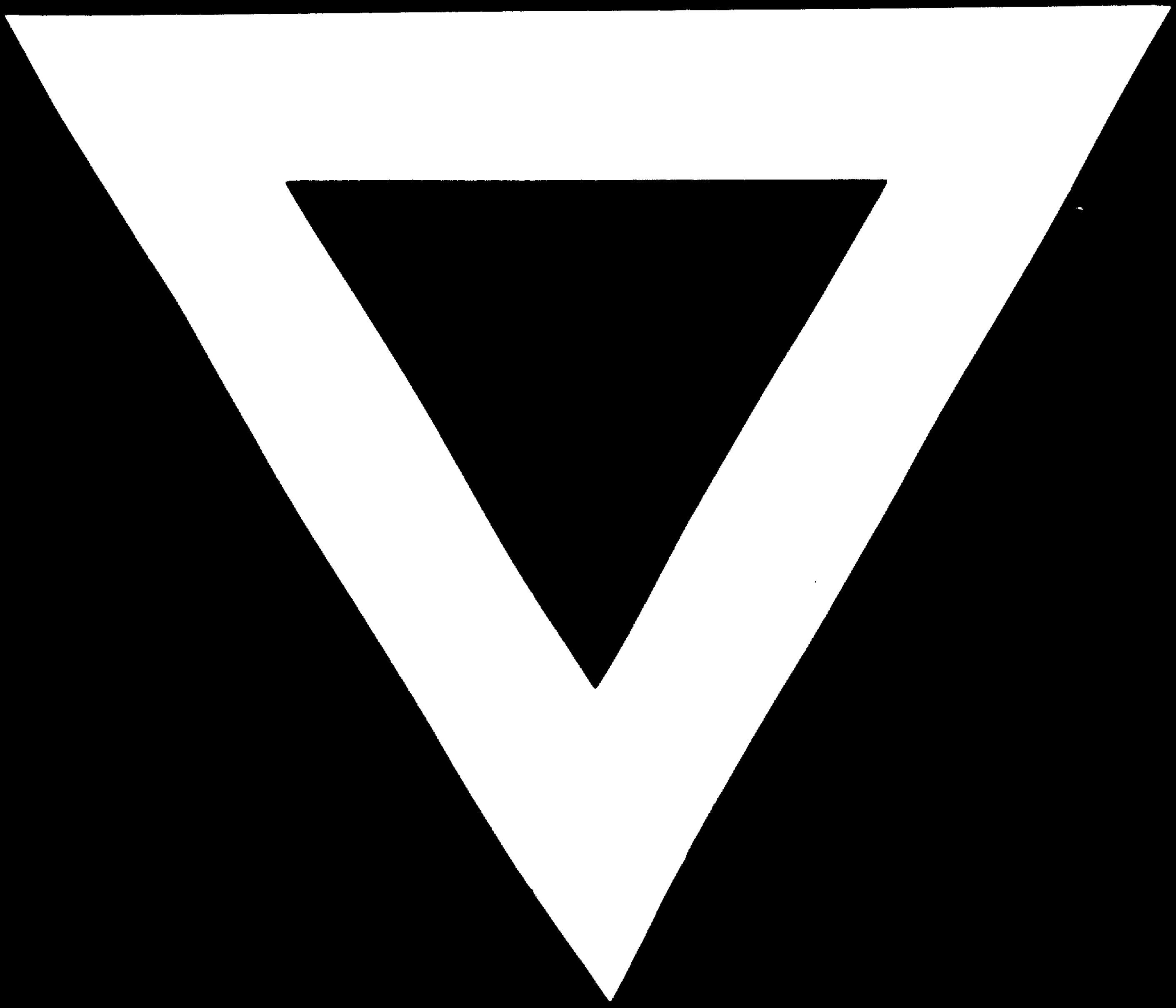
Fusion Cast Refractories. Although the melting point of refractory materials is high, it is possible to fuse them in electric arc furnaces and to cast the resulting liquid into moulds so that, on cooling, a shape, virtually non-porous and of extreme hardness, is produced.

The demand and applications for fusion cast refractories is increasing and many different compositions are now manufactured. These include alumina, mullite, magnesia, mag-chrome, zirconia, thoria. Fused silica is formed similarly, but unlike most others it is a true glass on cooling.

Refractories formed in this way are strong, hard and able to withstand enormous erosion and corrosion conditions. They have to be prepared carefully; long slow cooling is essential with seeding of the molten mass to ensure crystallisation, (not for fused silica). Thermal shock is frequently a serious problem, but otherwise fusion products are excellent though costly.

Refractory Whiskers and Fibres. Several methods have been developed for producing refractory materials in the form of thin continuous or long filaments. The techniques of fibre glass manufacture can be applied to a wide range of compositions and the fibrils so produced are super-refractory insulators, similar in structure to asbestos. Alumino-silicate compositions in fibrous form are in commercial manufacture.

Whiskers are fibres of extremely small cross-section. They are usually manufactured by growing the mineral species from a volatile phase at high temperatures. Carbon whiskers are well-known, boron also has exciting possibilities, but alumina and silicon carbide can likewise be produced in whisker form. The potential of these materials as reinforcement mats in metals and other ceramics to be used at high temperatures is being actively investigated at the present time.



74.10 . 2