



Presidential address: How cool are refractory materials?

by A.M. Garbers-Craig*

Synopsis

This paper reviews the history of refractory materials, highlights the development of refractory technology over the years, draws attention to the technology behind these materials, and comments on future developments in this field. By walking the path with refractory materials, from their initial uses in BC times, to the composite materials that are used nowadays, and the nanotechnology developments that are currently taking place in this field, the reader will come to agree that refractory materials are indeed very 'cool'!

Keywords: refractory materials; bricks; monolithic materials.

Introduction

Without refractory materials most of the scientific and technological inventions and developments we know today would not have been possible. The existence of virtually everything we see around us, or use in everyday life, is in some way dependent on refractory materials. Refractories are therefore facilitating or enabling materials, and are essential to the successful operation of any industry in which high temperatures are used^{1,2,3}.

The word 'refractory' is derived from the Latin word, '*refractarius*', which means stubborn⁴. These materials resist high temperatures, have high-quality mechanical and thermomechanical properties, have high corrosion resistance, act as a heat buffer between the walls of the containing vessel and the hot charge, and conserve process heat^{1,4,5}. Reliability and long service life are required from materials when put into operation. Refractory cost is therefore expressed in terms of tons of product produced, i.e. the cost of the refractory material is weighed against useful life and replacement cost.

A refractory material is a type of engineering ceramic called an 'industrial ceramic'³. Refractory materials, however, have coarser grain sizes and higher porosities than engineering ceramics, and consist of aggregate

particles, held together by a bonding (matrix) phase, where both the aggregate and the bond can be multiphased⁵. The particle size distributions are carefully controlled in order to control the microstructure, which directly influences porosity and density, strength, load-bearing capacity, corrosion resistance and thermal shock resistance⁵. A huge range of types of refractory materials, with a variety of intricate microstructures and phase assemblages, is commercially available.

Refractory materials are mostly oxide based materials, but they are becoming increasingly composite materials, which also contain non-oxide components such as graphite, SiC, resin and metallic particles^{4,5}. When refractories are classified on the basis of composition, a distinction can be made (according to the ISO [International Standards Organization Committee] classification) between basic, non-basic (or acidic), oxide-carbon and specialized materials (Figure 1)⁶.

Refractory materials are fabricated in two forms: shaped and unshaped (monolithic) refractories (Figure 2). Shaped refractories include fired and unfired materials with predetermined shapes, precast shapes and fusion cast refractories. Monolithic materials include plastic mixes, castables, ramming materials, dry vibratables, gunning materials, fettling materials, coatings and mortars⁷. Monolithic materials differ from refractory bricks in that they are not shaped and fired before use. They therefore do not have high energy requirements, are more readily available, take shorter times to install, can be repaired locally and require less manpower⁸.

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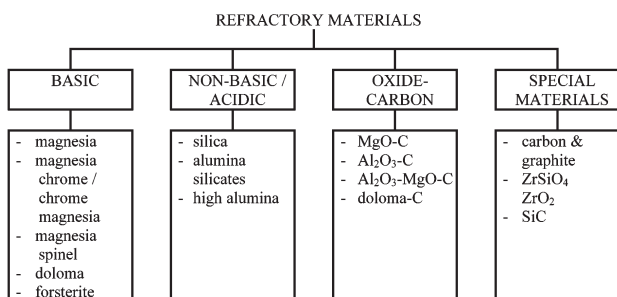


Figure 1—Classification of refractory materials, based on composition, according to the ISO classification⁶



Figure 2—Shaped (i) and unshaped or monolithic (ii) refractory materials⁹

The greatest use of refractory materials is the iron and steel industry (~70% of total use^{4,10}), while other significant consumers are the cement and lime, ceramic, glass, chemical, nonferrous and foundry industries (Figure 3). Consequently, any developments in iron and steel production technology have knock-on effects on the refractories industry.

A significant trend in refractories technology is the increased use of monolithic materials, which accounts for more than half of the total production in many countries, due to their quicker and cheaper installation, and to properties that approach those of formed products (Figure 4)^{11,12}. Monolithic materials have evolved over the years into a widely used class of refractory materials that offer performance and cost-effectiveness. Although refractory production in Japan has decreased over the period 1985–2004, the production of crude steel and monolithic refractories has remained fairly constant¹². This is due to the

decrease in unit consumption of refractories from 12 to 10 kg/ton of steel over this period, as well as the continuous increase in the amount of imported refractories, as refractory production is increasingly being done in developing countries, using low-cost workforces^{13,14} (Figure 5). This trend has also been followed by the US and Brazil. Over this period there has, however, been an increase in the production of castables and gunning mixes, and a decrease in plastics and ramming mixtures.

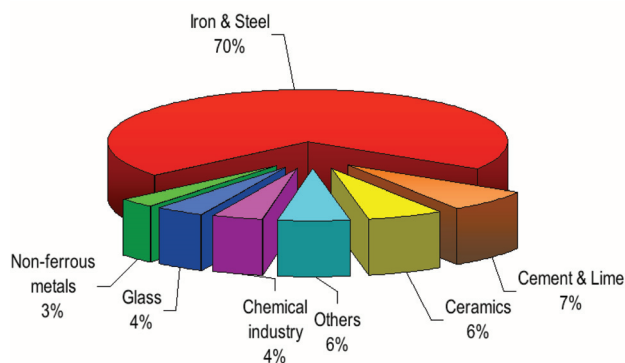


Figure 3—Global refractory market by end-user industries in 2003 (Vesuvius)¹⁰

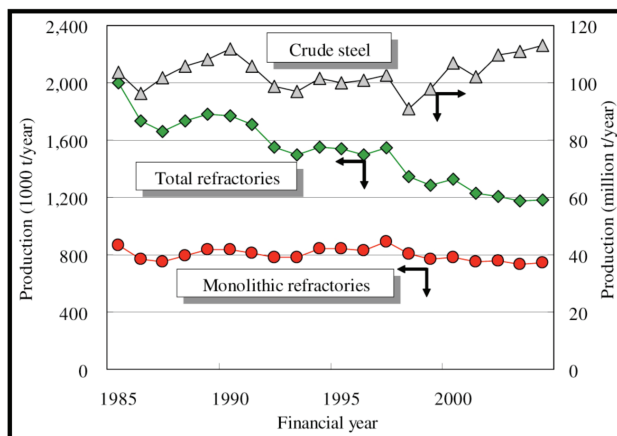


Figure 4—Trends in refractories technology and crude steel production in Japan, 1985–2004¹²

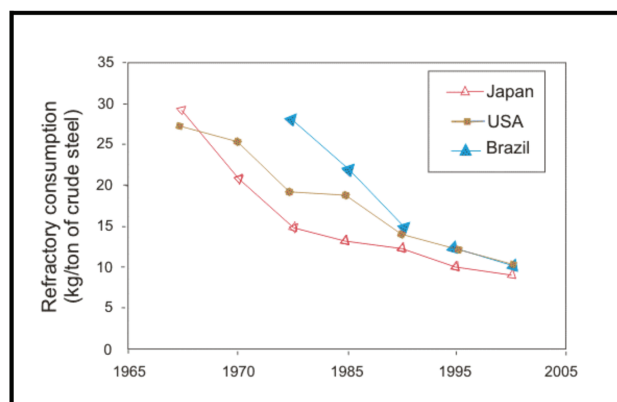


Figure 5—Refractory consumption in steelmaking, 1970–2000¹³

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Early years

Where did it all begin? The technological advancement of man started with the possession of fire¹⁵. This is also when the history of refractory materials started. Humans realized that certain areas became impermeable to water after being in contact with fire. Bigger fireplaces were built, and refractory technology evolved. The earliest baking oven found was in China, and dates back to ~30 000 BC. Baking ovens were also common in the Middle East by 10 000 BC¹. The earliest civilizations practised the art of pottery by forming and burning clay as long ago as ~6500 BC³. Archaeological evidence indicates that by 6000 BC the inhabitants of Western Asia already created vitrified clay hearths through pits dug in the earth to contain cooking fires¹⁶. Later people coated these hearths with wet clay to create a more heat-resistant surface and to repair cracks and spalls. This practice represented the first application of plastic refractories, whereby a ceramic bond was created through the use of process heat, in a refractory material formed on site. Evidence also exists that the ancient Greeks and Romans used mortars and concretes in processes where heat was involved. Kilns have been used by mankind for thousands of years. A kiln found in Tepe Gawra (an ancient Mesopotamian settlement in northwestern Iraq) is believed to have had a permanent roof as early as 4500–4000 BC¹⁷.

Natural rocks quarried into brick-like shapes, clays and sands served as refractory materials for thousands of years, while ovens were wood fired¹. Convective-draft and forced-draft furnace designs, which raised maximum temperatures to ~1100°C, were introduced around 4000 BC. By ~600AD porcelain was made in China at 1350°C. By ~1400 AD the earliest blast furnaces were operated in Europe at ~1500°C, fuelled mostly by charcoal. While iron could then be melted, treated and cast, stone and fireclay still served as refractory materials.

The earliest type of refractory material used in the US was mica schist or siliceous rock, which was used in iron furnaces or forges¹⁷. The first successful iron furnace was built in 1645 at Saugus, Massachusetts, using local stone. Stone was used for the building of furnaces and forges up to late in the nineteenth century because of the greater cost of firebrick. Even in 1968 stone was still used to line Bessemer converters.

Developments in refractory materials over the years

In this section the developments in the refractories industry over the centuries are discussed in terms of different types of refractory materials. Specific emphasis is put on silica, alumina silicates, magnesia, MgO-C and magnesia-chrome materials, as well as conventional castables, low cement castables and ultra-low cement castables. Technological advances have in general led to increased tapping temperatures, longer holding times and greater turbulence in the melt, which resulted in demands for higher grade and more resistant refractory materials, and improvements in application methods.

Silica

The first silica bricks are believed to have been made in ~1842 from Dinas rock in South Wales, a little later ganister

was used, and lime-bonded silica brick before 1858 in England¹⁷. In the US the first silica bricks were manufactured around 1866, although a patent for the manufacture of lime-bonded silica brick was already granted in 1858¹⁸. In 1957 silica was still the number one steel plant refractory, even though it was meeting severe competition from basic refractories, which have far higher melting points. The rise of the LD (Linz-Donawitz) or BOF (Basic Oxygen Furnace), which was first operated in 1952, resulted in the replacement of silica by basic refractories, resulting in dramatic drops in the production of silica bricks. Over the period 1947–1965 the production of silica bricks in the US dropped to a third, mainly owing to the obsolescence of the open-hearth furnace¹⁷.

Although silica bricks fulfilled their main purpose of withstanding high temperatures in the open-hearth furnace, they had some drawbacks: the bricks cracked and spalled when they were rapidly heated or cooled over low temperature ranges¹⁹. This is due to the fact that the raw material quartzite, which is used for the manufacture of silica bricks, undergoes various modifications with different densities and volume changes when heated. With increasing temperature α -quartz converts to β -quartz (stable to 870°C), which then converts to α -, β - and β' - tridymite (stable from 870°C to 1470°C) and then to α - and β -cristobalite (stable from 1470°C to 1723°C, the melting point)¹. These crystalline phases, as well as vitreous silica, all have extended temperature ranges over which they are metastable, as they all under cool. Inversions between α - to β -quartz or α - to β -cristobalite, which are associated with slight modifications in structure, are rapid, whereas the quartz to tridymite inversion is sluggish as it involves a major change in crystalline structure.

The rapid high-low cristobalite ($\Delta V \sim 1.8\%$), high-low quartz transitions ($\Delta V \sim 1\%$) and high quartz-high tridymite transitions ($\Delta V \sim 13\%$) are in the disruptive range¹. Due to the large volume change that occurs with cristobalite inversion, furnaces that are lined with silica bricks must be heated or cooled with extreme care in the temperature range where this inversion takes place, i.e. under 600°C (Figure 6). As the high temperature forms very low coefficients of expansion, silica bricks has almost zero expansion above 600°C. The

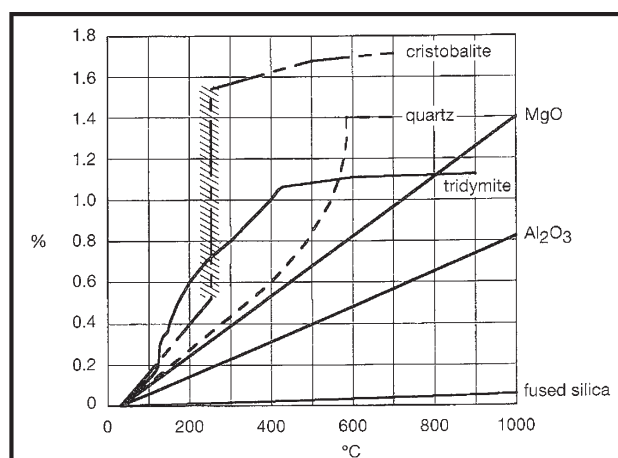


Figure 6—Percentage linear thermal expansion of polymorphic forms of silica minerals, magnesia and alumina as a function of temperature²⁰

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large expansion of SiO_2 brick below 400°C makes it unsuitable for use in the temperature range between room temperature and 600°C . A fired silica brick typically consists of tridymite, cristobalite, some residual quartz, as well as small amounts of pseudowollastonite (CaSiO_3) (which forms due to the addition of CaO as sintering agent and binder), and a glassy phase (the amount of which depends on impurity components such as alkali oxides and alumina)¹⁷. Silica bricks have high load-bearing capacity at high temperatures and therefore have been used widely in open-hearth furnaces, glass tanks, kilns and coke ovens³. Silica bricks are currently mainly used in by-product coke oven batteries and glass-melting furnaces.

Alumina-silicate and alumina materials

Alumino-silicate materials include fireclay (prepared from clay minerals, 25–45% Al_2O_3 , Figure 7), sillimanite, kyanite, and andalusite (prepared from alumina silicate anhydrides, 45–65% Al_2O_3 , Figure 8), mullite (65–75% Al_2O_3), bauxite (mixture of alumina hydrates, 75–90% Al_2O_3) and corundum (90–100% Al_2O_3) based materials¹⁸. Clay minerals are hydrous alumino-silicates with a layer structure, and develop plasticity when mixed with water³. Bricks are rarely made from only one raw clay, but the desired properties are generally obtained by the use of grog, or by the blending of one clay with another¹⁸.

Sillimanite, kyanite and andalusite are chemically identical ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), but with different crystal structures¹⁸. The end-product when heating these refractories is mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), cristobalite with some of the silica being present as a glass (Figure 9). These materials have a higher mullite content than the fireclay materials. The production of bricks from these minerals does not present specific obstacles. Mullite does not occur in nature as a material that can be mined, but is synthesized by heating alumina and clay to a high temperature. Sintered and fused mullite are available¹⁸. Alumina occurs mostly as $\alpha\text{-Al}_2\text{O}_3$ (rhombohedral), $\gamma\text{-Al}_2\text{O}_3$ (cubic), $\beta\text{-Al}_2\text{O}_3$ (appears to be formed where Na_2O , K_2O or CaO is present and may therefore rather be an aluminate)¹⁸. Refractory alumina is mostly produced from bauxite.

The depletion of conveniently located natural stone led to the production of hand-moulded fireclay bricks²¹. With the onset of the industrial age the production of bricks in mechanical presses started, while fairly high quality bricks were produced in downdraft kilns in the late 1800s¹⁸. The earliest direct reference to the manufacture of firebrick from US clay was in 1793¹⁷. The early kaolin bricks were prepared by a method of double burning, whereby mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), cristobalite and a glassy phase (which contained the impurity phases) formed¹⁷. From the early use of natural stone, and the use of clays and sand in ramming mixes it became clear that the chemical analysis of the natural material was of importance, as it was linked to its refractoriness²¹. For example, lighter coloured raw materials indicated lower concentrations of iron, and in general higher refractoriness. The modern era of the alumina silica brick started after the first publications of phase equilibrium diagrams after ~1920, when scientific principles guided the development of fireclay brick, rather than trial and error¹⁸. Sillimanite was once cut into blocks and used in glass tank furnaces without prefiring, but then it was realized that it is more economical to crush and grade it and make bricks,

mostly with a clay bond. The first bauxite deposits were discovered in the US during 1888¹⁷. World War II marked the development of bauxite-based materials in North America as an alternative to basic refractories that were all of a sudden not available from Europe any more²¹. The development of the Bayer process for the manufacture of aluminium also led to the manufacture of calcined and tabular alumina (Figure 9), and subsequently a new line of alumina brick. In the late 1970s and early 1980s alumina-silica brick consumption peaked and started to decline owing to the developments in refractory concretes or castables. Alcoa developed the procedure whereby 'tabular alumina' is produced by firing small spheres of calcined alumina at $\sim 2000^\circ\text{C}$, followed by crushing, whereby coarse crystalline α -alumina of very high density is produced¹⁸. In 1920 alumina-silica refractories were already prepared by fusion and casting¹⁷.

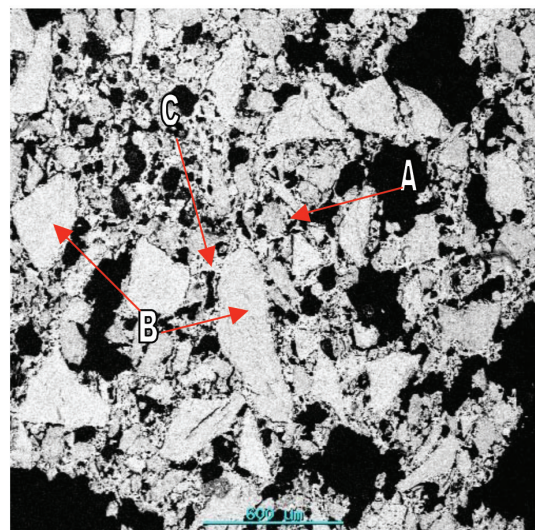


Figure 7—EBI of the typical microstructure of a porous fireclay brick. A= SiO_2 ; B=mixture of SiO_2 and mullite; C= $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-(K,Na)}_2\text{O}$ -based bonding phase

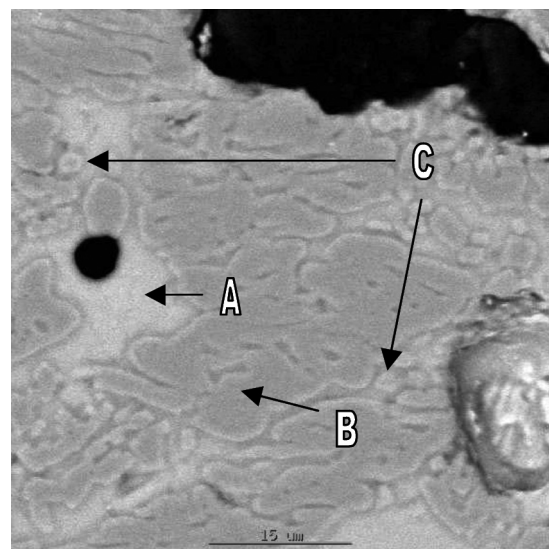


Figure 8—EBI of the typical microstructure of fired andalusite. A= $(\text{K,Na})_2\text{O-CaO}$ -iron oxide-rich glass; B=mullitised andalusite; C=andalusite fine

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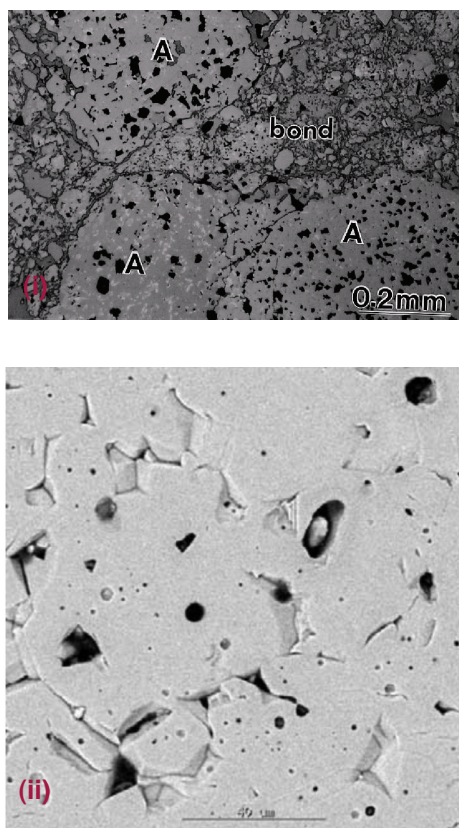


Figure 9—EBIs of typical microstructures of (i) a 80% alumina brick⁵ that contains calcined bauxite grains (A) and (ii) tabular alumina grains

Insulating materials

Asbestos has been used as fire-resistant cloth in Siberia as far back as the thirteenth century¹⁸. One of the breakthroughs in refractory development, however, came in the mid-1920s with the production of insulating firebrick¹⁷. Today commonly used insulating materials include perlite (an amorphous volcanic glass with high water content), diatomite or kieselguhr (small aquatic plant skeletons with silica as the main component), vermiculite ($(\text{Mg}, \text{Fe}^{++}, \text{Al})_3(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$, which on heating exfoliates, i.e. bursts into a large number of thin flakes that are separated by air spaces), anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), clay, silica, mullite, high alumina (e.g. bubble alumina) and ceramic fibre materials²⁰.

Ceramic fibre materials contain inorganic, non-metallic fibres, which could be either glassy or polycrystalline²⁰. They therefore contribute to energy savings in high temperature applications. The ceramic fibres are usually Al_2O_3 - SiO_2 and Al_2O_3 - ZrO_2 - SiO_2 based, while the glass fibres (also referred to as alkaline earth silicate fibres) contain CaO , MgO , Al_2O_3 and SiO_2 in various amounts.

Insulating materials are characterized by low thermal conductivity with good thermal shock resistance (due to their low porosities), low stored heat, resulting in decreased energy consumption, and shorter cycle times for furnaces that are operated intermittently²⁰. They also have low strength and abrasion resistance, and low corrosion resistance. For insulating firebrick the porosity is normally

created by adding combustible material (such as sawdust) to the raw material mixture³. On firing the sawdust burns out, and leaves a large fraction of interconnected pores within the material. Shaped heat-insulating materials have total porosities of $\geq 45\%$ by volume according to DIN EN 1094-220.

Magnesia

Unfortunately the nomenclature of MgO -based refractories is imprecise: the term 'magnesite' does not refer only to magnesium carbonate (MgCO_3), but also to the fired carbonate²². The same name is therefore used for both the carbonate and the oxide. The situation was confused even further by using the term 'magnesite' for synthetic magnesia extracted from brines or sea water through the precipitation of $\text{Mg}(\text{OH})_2$. The term 'periclase' is in general reserved to describe crystalline MgO . Magnesium oxide raw materials and products are, however, interchangeably referred to as MgO (chemical formula), magnesia (chemical name), periclase (mineral name) and magnesite (mineral name for MgCO_3)²³.

Magnesite products were produced for over a hundred years from breunnerite minerals (solid solution of MgCO_3 and FeCO_3 , yielding 4–8% Fe_2O_3 in the dead-burned product)¹⁸. As a lining material for steelmaking furnaces MgO was already suggested in Europe as early as 1860, but it came into regular use only in 1880¹⁷. In that year the first refractory magnesite was mined at Veitsch, Austria. From 1888 the use of magnesite increased rapidly as the advantages of the basic steelmaking process over the acid process became evident. The earliest reference to chemically bonded basic refractory was made in 1905, referring to sodium silicate and calcium chloride²². 1935–1941 saw the patenting of chemically bonded bricks, which included sulphate, sodium silicate sulphite lye and small additions of clay or bentonite. In 1941 a patent was published describing a process during which U-shaped steel sheets were placed in the press mould whereby the resultant brick was encased in steel on four sides. When heated the plates (usually mild steel) slowly oxidized, thus expanding and reacting with the periclase to form magnesioferrite, which encouraged the intergrowth of periclase across the original brick surface, producing a near monolithic structure. The production of basic refractories over the period 1947–1965 increased sixfold in the US, due largely to their use in the basic oxygen converter and the growth of high-grade plastics and castables¹⁷.

A small sea water plant already existed in France as early as ~1890, but sea water magnesia was produced in the US only by 1931, by the California Chemical Company. Production of magnesite from brines, bitterns and sea water grew rapidly during the 1940s, and by 1973 large portions of refractory magnesia used in the UK, US and Japan came from sea water magnesia plants¹⁸. Direct-bonded basic brick with low impurity content has been made since the late 1950s, as were basic fusion-cast blocks. During the early 1960s it became clear that qualities of higher purity and density were required. This was achieved by dead-burning (made 'unreactive', i.e. without tendency to hydrate, carbonize or shrink) in a rotary kiln at temperatures above 1800°C , whereby B_2O_3 is volatilized and high-density large grains are produced¹⁸.

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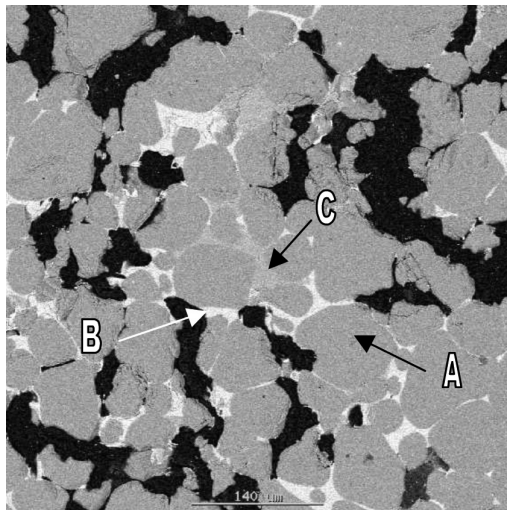


Figure 10—EBI of a forsterite-bonded MgO brick. A=MgO; B=monticellite (CaMgSiO_4); C=forsterite (Mg_2SiO_4)

The greatest quantity of magnesia refractories is used in the steel industry²³. The types and amounts of these materials have changed over the years as steelmaking technology has developed. The major application of magnesia refractories in the 1950s and 1960s was in open-hearth furnaces.

The properties of burned periclase or magnesite brick may vary widely depending on its CaO/SiO_2 ratio, the amount of impurities such as Fe_2O_3 , Al_2O_3 or B_2O_3 , and the temperature to which the brick was fired²⁴. Magnesia bricks based on sintered magnesia usually contain either a forsterite or dicalcium silicate bond to obtain a high hot strength (Figure 10)²⁰.

The main reasons for the success of magnesite are its high melting point (2800°C) as well as excellent resistance to attack by iron oxide through solid solution phase formation (Figure 11²⁵) and high-lime fluxes¹⁸. Its principal limitations are its high thermal expansion (Figure 6), which makes the production of bricks with high thermal shock resistance

difficult, and their tendency to shrink when exposed to high temperatures for long periods of time²².

Oxide-carbon refractory composites (with emphasis on magnesia-carbon)

The corrosion resistance of a refractory material that consists only of oxides can be improved by reducing its porosity, i.e. increasing its density²⁶. However, when the porosity becomes too low, the thermal shock resistance of the refractory is also low. The design of a refractory material that has a high thermal shock resistance as well as excellent corrosion resistance is therefore a matter of a delicate balance. Adding carbon to the oxide-based material solves the problem, as carbon has low thermal expansion and high thermal conductivity (thereby forming a material with high thermal shock resistance) and is not wettable by slags (thereby increasing the corrosion resistance of the oxide-based material) (Figure 12)²⁴.

C-bonded bricks are primarily used in the steel industry⁵. Carbon, as a bonding phase and as graphite flakes, is added to basic bricks, alumina, zirconia and silica. Either a carbon bond (derived from the pyrolysis of pitch ore resin) or a ceramic bond (derived from clay, or metallic or ceramic additives) is used to bond the oxide and graphite in the oxide-graphite refractories. High graphite levels are used to maximize thermal conductivity, whereby the use of water cooling systems are facilitated. Oxide-graphite refractories may contain from 4–30 wt% natural graphite as well as carbon from the pitch or phenolic resin binder.

Historically pitch-containing basic refractories have been used in basic Bessemer since the late 1800s²⁴. The first refractory materials were pressed from dead-burned doloma and pitch or tar, because of the low softening points of these binders. The development of the BOF in the late 1950s and early 1960s introduced pitch-bonded doloma, doloma-magnesia, magnesia-doloma and magnesia brick²³. In the late 1960s high-strength pitch-impregnated, burned magnesia bricks were developed, as well as magnesia and doloma gunning materials for maintenance. By 1970 the pitch-containing refractories in the large top-blown BOF

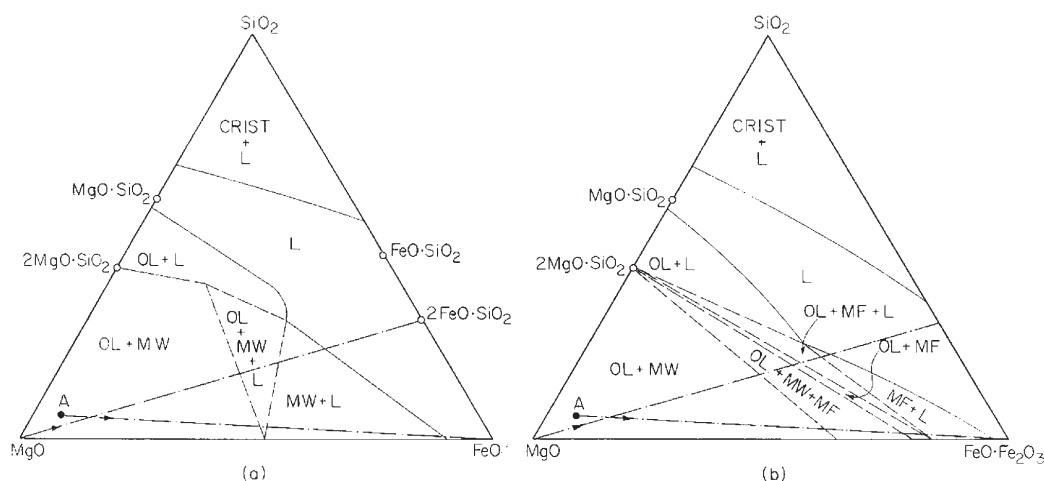


Figure 11—1650°C isothermal sections through the SiO_2 -MgO-iron oxide system in contact with metallic iron (a) and in air (b)²⁵

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furnaces in the US were made from a variety of basic refractory raw materials bonded or impregnated with high-temperature pitches. All the refractory raw materials used came from the MgO-CaO system, as these raw materials are most resistant to BOF slags²⁴. These included periclase and doloma, although the low hydration resistance of doloma imposed limitations on the use of this brick. The pitches used were by-products from the distillation of bituminous coal, with low volatile content for limited fuming during manufacturing, and high precipitate for a maximum possible amount of carbon in the brick. By 1970 pitch-bonded, tempered and burned-impregnated bricks were manufactured for the BOF. Tempering was mostly done at temperatures between 200°C and 300°C in muffle-type furnaces. During tempering pitch migrates through the brick to impregnate most of the intergranular and intragranular porosity, and coats the surfaces of the grains, thereby improving the low-temperature hot strength and hydration resistance of doloma brick.

Pitch-impregnated bricks are produced by forcing pitch into the open pores of a burned brick, by simply dipping the brick into liquid pitch or through a vacuum-pressure system, which accelerates the rate at which pitch is forced into the brick. Fractional distillation of the pitch during service results in the deposition of residual carbon in the pores of the brick, which graphitizes to some degree during heat-up of the BOF.

The Japanese introduced resin-bonded magnesia-carbon bricks for hot spots in the EAF in the mid-1970s, with graphite becoming the main carbon ingredient in these bricks²⁵. This type of brick was also introduced to the BOFs in the early 1980s, which consequently almost doubled steelmaking refractory life. It was found that carbon addition reduces slag penetration (thereby increasing corrosion resistance), reduces the elastic modulus and increases thermal conductivity (thereby increasing thermal shock

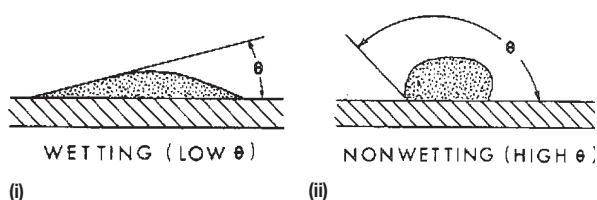


Figure 12—Illustration of wetting of a brick to which carbon was not added (i), and to which carbon was added (ii)²⁴

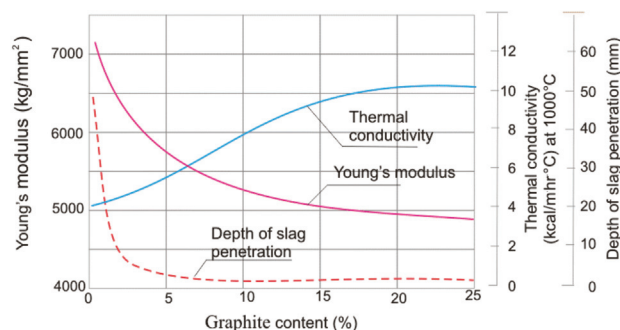


Figure 13—The effect of graphite on MgO materials²⁷

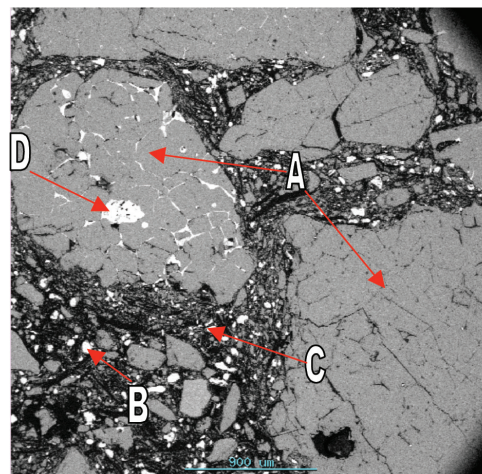


Figure 14—EBI of the typical microstructure of a MgO-C brick which contains Al and Si as antioxidants. A=MgO; B=aluminium; C=silicon; D=merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$)

resistance) (Figure 13)²⁷. A period of further developments in and experimentation with zoning of magnesia-carbon-based bricks started.

The addition of carbon to oxide-based materials led to the question of how carbon can be protected from oxidation. This has been addressed by adding non-oxides such as metal, alloy and carbide particles to the refractory mixture, where they perform a self-repairing function. These non-oxides include Al, Si, Al-Si, Al-Mg alloy, SiC, B_4C and Si_3N_4 , and are called antioxidants²⁶ (Figure 14). These antioxidants preferentially react with air, form refractory phases on oxidation and further densify the refractory. The carbides also deposit free carbon in the refractory. Limitations on the use of Al as antioxidant include the tendency of Al_4C_3 to hydrate, and the fact that it cannot be added to an MgO-C monolithic material since Al particles readily react with H_2O of the binder²⁸. Alternative antioxidants to Al in MgO-C include $\text{Al}_4\text{O}_4\text{C}$, Al_2OC , $\text{Al}_8\text{B}_4\text{C}_7$ and Al_4SiC_4 . R&D on antioxidants is continuing. Binding resins that contain antioxidants attached to its polymeric chain in the form of complexation cations have also been investigated²⁹.

Chrome-containing refractories

Magnesia-chrome and chrome-magnesite

The first documented evidence of experimentation with chrome ore as a refractory material was in 1879 in the open-hearth furnaces at Terre-Noire, France³⁰. Chrome ore was used on a larger scale in the furnaces of Petersburg-Alexandrofky Steelworks in 1880, when crushed chrome ore was mixed with tar and used as a partitioning agent between calcined dolomite and silica bricks in the hearths of open-hearth furnaces^{18,30}. By 1886 blocks of chrome ore, laid in a mortar of chrome ore fines and lime, were used at a number of European open-hearth plants to line walls and hearths, while a mixture of chrome ore and tar was used as taphole materials. In the late 1880s chrome ore as a hearth material for open-hearth furnaces was replaced by magnesite. The first recorded use of chrome bricks in England was in 1886,

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while the use of chrome ore as a refractory material began in the US in ~1896³⁰.

Chrome-magnesite refractories date from the early 1930s, when these developed simultaneously in Germany, Great Britain and the US³¹. The use of chromite as a neutral refractory was limited to low temperatures as it tended to soften and collapse under load and was sensitive to thermal shock. Silicate-bonded magnesia bricks, on the other hand, have high thermal expansion coefficients and poor thermal spalling resistance⁵. By developing this composite material, a brick of superior high temperature strength and resistance to deformation with improved thermal shock and spalling resistance was produced³¹. By ~1935 the production of both fired and chemically bonded (sodium silicate, sodium bisulphate, sulphuric acid) MgO-chrome refractories was established²². Compositions with a bias to chrome-magnesite were favoured, with main uses in the back and front walls of open-hearth furnaces. These materials were relatively volume stable at high temperatures and insensitive to thermal shock. Though chemically basic, and therefore resistant to basic slags (e.g. in the open hearth), they could tolerate direct contact with silica. Steelmakers realized that these bricks offered the possibility of increasing production rates by increasing roof temperatures to above 1650°C, which is the limit of silica bricks. Basic roofs were first tested in Germany and Austria in ~1933, and used throughout World War II. After World War II the push for steel production from existing open-hearth furnaces pushed the silica bricks in the roofs to beyond their capabilities³². The introduction of oxygen into open-hearth furnaces also increased operating temperatures to the extent that silica could no longer compete with magnesite-chrome refractories. After 1960 the need for a low silica content in the magnesia-chrome brick became apparent. The addition of magnesite fines to chromite resulted in a product that was superior to chromite and magnesite refractories, as the addition of magnesite converted low melting magnesium silicates to forsterite (Mg_2SiO_4) (Figure 15)²⁵.

Chrome ore consists mainly of the mixed spinel

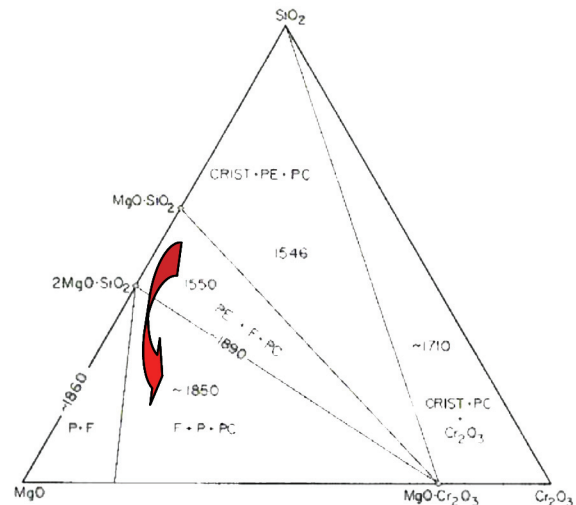


Figure 15—Solidus projection of the SiO_2 - MgO - Cr_2O_3 phase diagram which explains why the addition of MgO to chromite increases the solidus temperature (and therefore refractoriness) of the MgO-chrome brick²⁵

(Mg,Fe^{2+})O.(Cr,Al,Fe^{3+}) $_2\text{O}_3$, and have high melting points, in excess of 1800°C^{18,22}. Although the iron in the chrome ore can exist in both divalent and trivalent states, FeO is the common form. A major manufacturing problem of composite basic refractories in the 1930s was the large firing expansions, which gave products high porosity and low mechanical strength²². It turned out that susceptible chrome ores in composite bricks could be oxidized during the early stages of firing and reduced at a later stage in the firing cycle. In these spinels the divalent cations Mg^{2+} and Fe^{2+} form a magnesium spinel and a sesquioxide solid solution (Fe,Al,Cr) $_2\text{O}_3$ during oxidation. Subsequent reduction converts the Fe_2O_3 to FeO, giving solid solution effects, which result in large increases in volume. Bricks that are friable and porous consequently form. High Al_2O_3 content was found to reduce the susceptibility of ores to oxidation (Figure 16)³³.

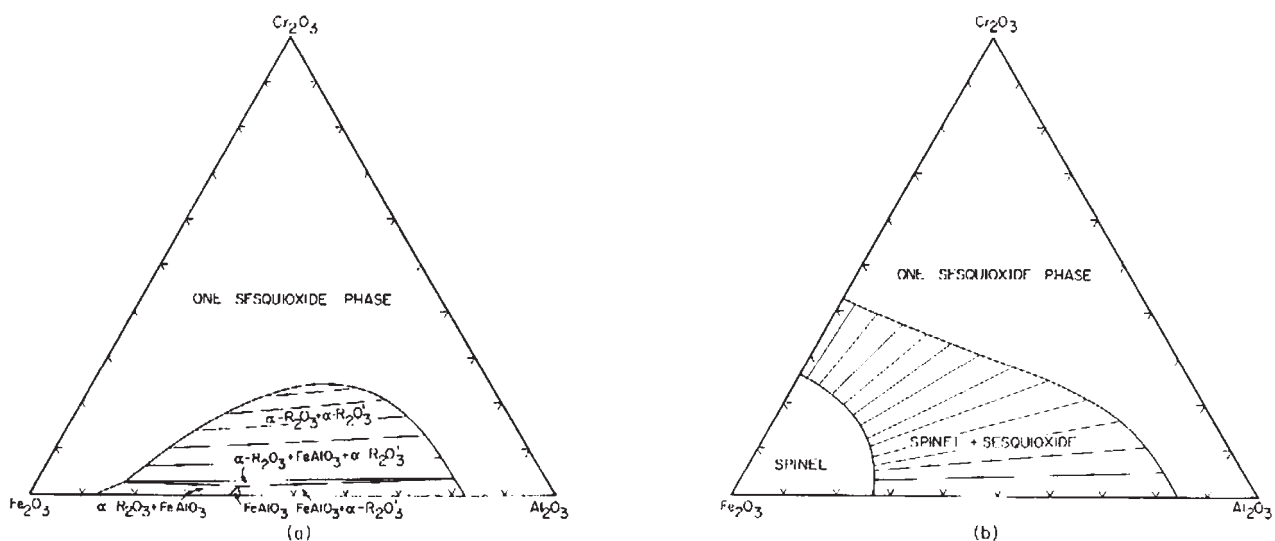


Figure 16—Isothermal sections through the system iron oxide- Al_2O_3 - Cr_2O_3 in air at (a) 1250°C and (b) 1500°C³³

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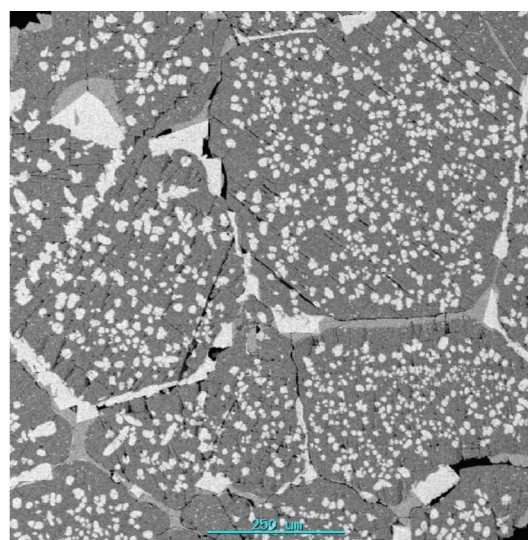
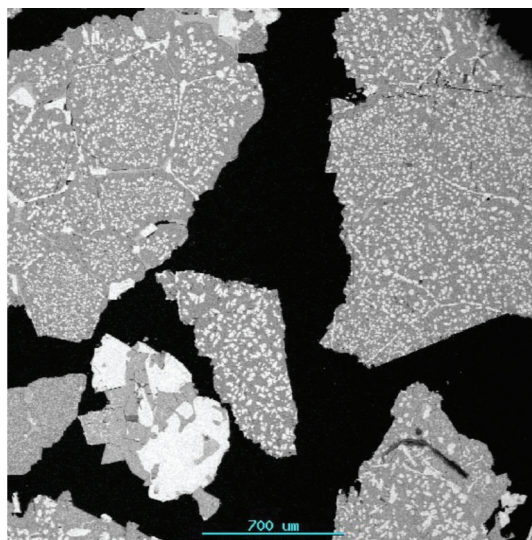


Figure 17—EBI of the typical microstructure of fused MgO-chrome grains. Dark grey phase: MgO; grey phase: silicate impurity; light grey phase: spinel

By 1937 it was clear that the major cause of wear of composite basic bricks was a slabbing-off or successive loss of layers of up to ~7 cm from the working face when iron oxide was absorbed by the bricks at high temperatures²². This process is called 'bursting', which is accompanied by an increase in porosity. The bursting expansion results from the solid solution of magnetite (Fe_3O_4) in the granules of the chrome spinel, which is accompanied by an increase in porosity. A large bursting expansion occurs when the spinel mixture contains Fe^{2+} , Fe^{3+} and Cr^{3+} . The substitution of Cr^{3+} for Al^{3+} , or Fe^{2+} for Mg^{2+} produces a substantial increase in the bursting expansion.

Secondary spinel, observed for the first time by Berry *et al.* when they studied chemical changes in basic brick during service, was to become a feature of the direct-bonded brick that developed in the late 1950s^{22,34}. Through impurity content and grading control improved thermal shock and corrosion resistance were obtained¹⁸. In these bricks silicate films that typically surrounded chrome ore particles and periclase grains were replaced by direct periclase-spinel and periclase-periclase bonds, when the bricks were fired up to 1800°C¹⁸. The direct bond develops on cooling either by precipitation of spinel from solid solution in the periclase or by the crystallization of periclase and spinel from solution in liquid silicates at high temperature²². Direct bonding confers high hot strength and density, and therefore high slag penetration resistance⁵.

By the late 1960s it became customary to include a proportion of chrome ore fines, in order to achieve direct bonding²². In 1962 the rebonded fused-grain basic refractory was introduced in the US³². The grain used to manufacture rebonded fused-grain materials is made by fusing a mixture of magnesia and chrome ore in an arc furnace at temperatures around 2450°C. Microstructurally the rebonded fused-grain brick is composed of large fused aggregates that are imbedded in a matrix of finer fused grains, with mostly direct periclase-periclase or periclase-spinel bonds (Figure 17). The introduction of the AOD process during this time also found usage of these direct-bonded and rebonded fused-

grain magnesia-chrome bricks²³. Excessive expansion during firing and bursting expansion do not arise with the fast firing to high temperatures used to produce direct bonds.

In 1952 the first fused cast magnesite-chrome was produced, mainly for use in the steel industry. In general these fusion-cast materials are denser than the fired product (low porosity), have higher slag resistance, a high abrasion resistance, but not a high thermal shock resistance^{5,18}.

The replacement of chrome-magnesia and magnesia-chrome bricks with burned magnesia-spinel bricks started approximately 34 years ago, due to environmental concerns related to Cr(VI) formation^{4,23}. This trend was accelerated after 1986.

Other chromium oxide-containing refractory materials

Other chromium oxide-containing refractory materials that have been produced over the years include chrome-silica, chrome-alumina, alumina-chrome, chrome-olivine, chrome-doloma, and chrome-containing AZS materials^{18,35}. In the Al_2O_3 -containing materials part of the Al_2O_3 is replaced by Cr_2O_3 , which leads to the formation of $(\text{Al,Cr})_2\text{O}_3$ solid solution crystals on firing²⁰.

High temperature oxidation of Cr_2O_3 and chromite, particularly in the presence of alkali oxides, poses the danger of Cr(VI) formation. Cr(VI) is highly soluble in water, and would therefore pose an environmental risk if these linings are simply dumped after service at high temperatures¹.

Magnesia-spinel

Legislation on the disposal of Cr-containing materials has led to the development of MgAl_2O_4 spinel-bonded MgO bricks⁵. These bricks have high corrosion resistance, improved strength at high temperatures and better thermal shock resistance than MgCr_2O_4 -bonded bricks. By comparing the $\text{MgO-MgAl}_2\text{O}_4$, $\text{MgO-MgCr}_2\text{O}_4$ and $\text{MgO-MgFe}_2\text{O}_4$ phase diagrams (Figure 18) it is clear that aluminium ions are much less soluble in the periclase lattice at high temperatures than Cr_2O_3 and Fe_2O_3 , and less exsolution-dissolution of the spinel phase occurs during temperature fluctuations³⁶.

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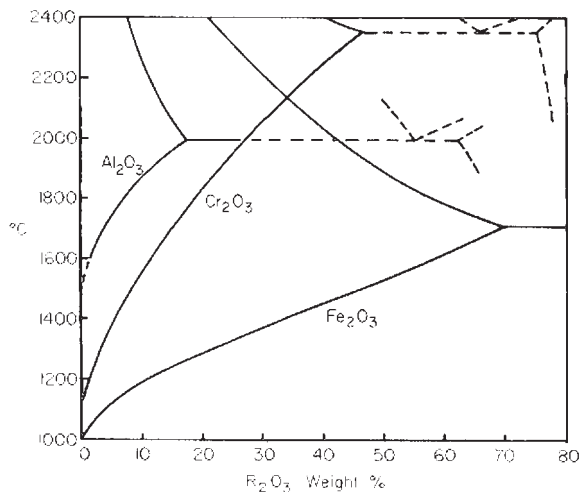


Figure 18—Comparison of phase relations in the systems MgO-MgAl₂O₄, MgO-MgCr₂O₄ and MgO-MgFe₂O₄³⁶

MgAl₂O₄ also has a lower vapour pressure at high temperatures. MgO-MgAl₂O₄ fused refractories are therefore more stable during temperature change than MgO-MgCr₂O₄ and MgO-MgFe₂O₄. However, MgO-MgAl₂O₄ refractories do not have as good a corrosion resistance to steelmaking slags as do MgO-MgCr₂O₄ refractories, as chrome-containing compounds are much less soluble in silicate-containing melts than alumina-containing compounds.

The first MgO-MA (MgO-MgAl₂O₄) bricks were made in the 1960s, during which a small amount of alumina or bauxite powder was co-milled with MgO powder, and added to MgO bricks³⁷. These MgO-MA bricks had higher hot strength and much better thermal shock resistance than the silicate bonded magnesite bricks. The Al₂O₃ content was limited to <10 wt% in these first generation MgO-MA bricks,

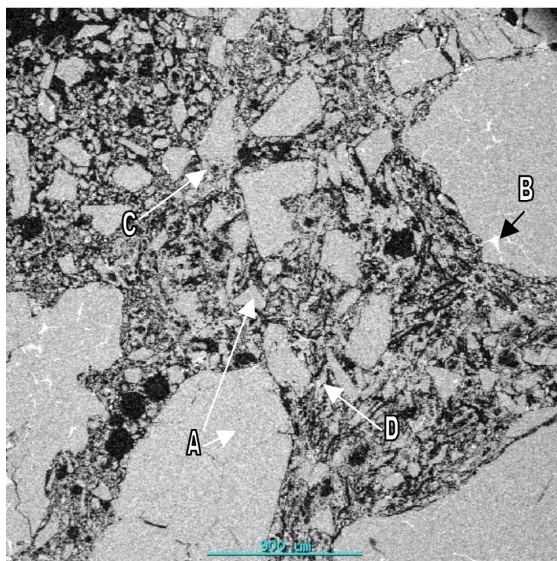


Figure 19—EBI of the typical microstructure of a spinel-bonded MgO-MA brick. A=MgO; B=merwinite (Ca₃MgSi₂O₈) impurity phase; C=MgAl₂O₄ bonding phase; D=monticellite (CaMgSiO₄) impurity phase

as although increasing Al₂O₃ additions led to better thermal shock resistance, it increased the porosity of the brick, and made it difficult to produce dense bricks. The second generation of MgO-MA bricks was developed in the mid-1970s, and used preformed synthetic spinel grain to replace some of the MgO. In this way a larger amount of MgAl₂O₄ could be added to the brick without drastically increasing the porosity. The third generation of MgO-MA bricks contains spinel aggregates and spinel in the matrix via addition of preformed spinel and/or alumina powder to form *in situ* spinel (Figure 19). These bricks have higher hot strength, higher slag penetration resistance, higher thermal shock resistance and a longer service life.

Spinel-containing refractories are classified into MgO-Al₂O₃, MgO-Al₂O₃-TiO₂ (TiO₂ addition reduces slag wettability, i.e. leads to the suppression of slag penetration and enhances corrosion resistance), MgO-Al₂O₃-ZrO₂ (ZrO₂ enhances hot strength, thermal shock resistance and improves corrosion resistance), MgO-Al₂O₃-SiO₂, MgO-Al₂O₃-CaO and MA-carbon refractories.

Doloma

Doloma refractories are potentially high-quality refractory materials due to their thermal and chemical stability, chemical resistance against basic slags and coatability in the cement rotary kiln³⁸. Two major shortcomings are their low hydration resistance and low thermal shock resistance.

The use of dolomite (CaMg(CO₃)₂) as a refractory started in ~1878 when dolomite rock was used as lining material in Thomas converters¹⁸. The stone was bonded with sodium silicate and calcined *in situ*. This consumable dolomite hearth was later replaced with linings of tar-bonded doloma of low purity. Only in the 1930s could satisfactory fired bricks be produced. A large portion of doloma refractory technology was developed in England during World War II, due to increases in breakouts from open-hearth furnaces when they were held for many hours after being ready to tap, in order to avoid glare during air raids or anticipated air raids. Tight control was required during manufacturing in order to prevent hydration, as well as to prevent the β dicalcium silicate from converting to γ dicalcium silicate on cooling with a 10% volume increase (a process called dusting). Medium and high-purity tar-bonded and direct-bonded doloma bricks were used in LD converters and electric furnaces during the early 1950s³⁹. Fired doloma bricks were developed for use in the burning zone of rotary cement kilns in the early 1960s.

Doloma is chemically compatible with the cement-making process, forms a protective coating with the clinker in the burning zone, and provides a chrome-free assembly. Doloma-based linings also bestow high desulphurization efficiencies during steelmaking and have good slag resistance to slags that are not completely saturated with lime, as a dense layer of Ca₂SiO₄ forms at the hot face, which limits further slag penetration³⁹. Slags deficient in CaO but enriched in R₂O₃ oxides (Al₂O₃, Fe₂O₃) are, however, highly corrosive to doloma brick due to the formation of low melting calcium aluminates and/or calcium ferrites.

Direct-bonded doloma bricks are produced by using organic binders that burn out during firing, thereby forming

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a direct bond through the lime phase³⁹. These bricks are prone to thermal shock, which is improved through the addition of small amounts of ZrO_2 . Carbon-bonded doloma bricks for steelmaking applications include pitch-bonded and resin-bonded bricks. In the 1990s trials on doloma graphite SENs and ceramic-bonded doloma tundish nozzles were started, to investigate whether the clogging of nozzles during the continuous casting of aluminium killed steels can be prevented.

Carbon refractory materials

All carbonaceous linings are thermally conductive rather than insulating⁴⁰. Sufficient cooling must therefore be applied to these lining systems in order to maintain refractory temperatures below the critical temperature at which chemical reactions such as oxidation, alkali attack, CO degradation or the dissolution of carbon by molten metal takes place.

Until the early 1940s carbon bricks were largely manufactured in Germany and the USSR¹⁸. The fact that carbon bricks must be fired under reducing conditions was the main reason for the slow development of these bricks.

Carbon black and graphite are the major sources of carbon added to refractories²³. Carbon blacks are formed by thermal decomposition of natural gas in the absence of air. Graphite developed naturally from carbonaceous sediments, and is classified into flake, crystalline and amorphous graphite. Carbonaceous materials used as refractories in freeze linings for submerged arc furnaces include carbon, semigraphite, semi-graphitized carbon and graphite⁴¹. Carbon, formed carbon, manufactured carbon, amorphous carbon and baked carbon refer to products constituted from carbonaceous filler materials such as calcined anthracite coal, petroleum coke or carbon black with binders such as petroleum pitch or coal tar. These mixtures are formed by moulding or extrusion, after which they are fired to temperatures of 800–1400°C to carbonize the binder.

The final product contains carbon particles with a carbon binder. Semigraphite is composed of artificial graphite particles that are mixed with a carbonaceous binder such as pitch or tar and baked at temperatures of 800–1400°C. The product consists of carbon bonded graphite particles. A semi-graphitized material is a fired carbon material that has been further heat-treated to temperatures between 1600 and 2400°C. The final product consists of carbon particles with a carbon binder, which are both semigraphitized, since the firing temperature is still below graphitization temperatures. Graphite occurs in nature in flake form. Synthetic, artificial or electro-graphite refers to a carbon material that has been heated to temperatures of 2400–3000°C. The final product consists of graphitized particles as well as a graphitized binder.

Carbonaceous ramming materials are extensively used with carbon bricks and blocks¹⁸. In the unfired state it is sufficiently deformable to help take up stresses due to thermal expansion. Tar is the most common binder, but a clay/water bond is also used. Many of the tar-based mixes used to require preheating to 60–70°C in order to reduce the viscosity of the binder and enable efficient ramming. Because of unpleasant fumes that were expelled, these types of rammables were replaced in the 1970s with rammables that do not require preheating to temperatures above 15°C.

Up to the 1970s carbonaceous cements were based on metallurgical coke, calcined anthracite and graphite (electro or flake), with ball clay added for plasticity and air-setting binders for green strength. In the early 1970s high-strength resin-based cements were introduced, which cure and carbonize, whereby strength develops.

Special refractory materials

Special refractory compositions are more expensive than fireclay or basic brick, and are used only when required. The most common special refractories include zircon ($ZrSiO_4$), zirconia (ZrO_2), AZS and silicon carbide (trade name carborundum).

The high melting point of ZrO_2 (>2500°C) and its chemical inertness make it a potential refractory material⁵. However, this is only viable if ZrO_2 is stabilized in its cubic structure by MgO or CaO addition, whereby the monoclinic-tetragonal transformation (which is accompanied by a large volume change) is avoided. Full stabilization in the cubic structure, however, also leads to increased thermal expansion, and along with its low thermal conductivity, decreases its thermal shock resistance. It was consequently discovered that partial stabilization of ZrO_2 improved its thermal shock resistance. This led to the use of partially stabilized zirconia (PSZ), which is a mixture of cubic and monoclinic zirconia, as a refractory material, although to a limited extent due to its relatively high cost. High zirconia refractories are not easily wetted by molten glass, and are therefore used in glass tanks when melting highly corrosive glass compositions.

SiC refractories have excellent thermal shock resistance (due to their low thermal expansion coefficient and high thermal conductivity), which makes them suitable for various refractory applications, particularly where cooling systems are used⁵. The high hardness of α -SiC also makes it very resistant to abrasion. A major implication of silicon carbide refractories is the tendency of these materials to oxidize at high temperatures, whereby a siliceous phase(s) forms³.

SiC was first commercially made by Acheson in 1891 by electrically heating petroleum coke, silica sand, sawdust and salt¹⁸. During the process the silica is reduced to silicon, which reacts with the coke, the sawdust burns out but keeps the mass porous to allow the escape of the gases, and the salt helps to volatilize impurities. Silicon carbide bricks and shapes were made by adding a plastic fireclay slip to a graded mixture of SiC grains, which was then shaped (pressed/tamped/isostatically pressed/moulded) and fired at temperatures of at least 1300°C. On firing a silicate liquid formed through the reaction of amorphous silica (from oxidation of SiC) with alumina-silicate from the clay, which on cooling formed a mullite and glassy bond between the SiC grains. This resulted in a volume increase and made it difficult to produce shapes to close dimensional tolerances, as well as causing some loss in thermal shock resistance. This has been overcome by forming either a nitrogen-bonded material or producing a self-bonded silicon carbide or a pyrolytic silicon carbide.

Nitride-bonded SiC is made by mixing α -SiC grain, Si metal powder and a temporary binder, and firing at 1350–1600°C in a controlled N_2 atmosphere, whereby a silicon nitride (Si_3N_4) grain boundary bond forms⁵. Heat treating in an N_2 - O_2 atmosphere can lead to oxynitride-

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bonded brick or sialon-bonded brick due to the reaction of the impurities in the SiC or deliberate addition of aluminosilicates. Sialon-bonded SiC has improved strength and alkali resistance compared to conventional nitride/oxy-nitride-bonded SiC.

Studies have also been conducted on TiO₂ additions to various refractories such as MgO-C (Al antioxidant), Al₂O₃-ZrO₂-C (Al and Si antioxidants) and Al₂O₃-Mg-PSZ (MgO partially stabilized zirconia)⁴². In these materials titania accelerates interaction between oxide, non-oxide, graphite particles and resin at low temperatures, and contribute to improved thermal shock resistance. This is due to the *in situ* formation of new phases (such as nanoscaled Ti(C,N) in the MgO-C; incorporation of TiO₂ in the zirconia lattice in the Al₂O₃-ZrO₂-C and Al₂O₃-Mg-PSZ, but also ZrO₂-TiO₂-Al₂O₃ melt in the Al₂O₃-Mg-PSZ) and/or the formation of microcracks that resist crack propagation.

Monolithic materials

The need for monolithic, joint-free refractories arose from the problems associated with traditional brick-mortar refractory constructions¹⁶. Significant developments in monolithic materials have been driven by more severe demands placed on them by consumers. Advances took place in the type and quality of the binders, aggregates and additives, and to innovations in their design and installation¹¹. Castables and gunning materials are the most abundantly used monolithic materials¹².

Monolithic materials first appeared in the US as distinct refractory materials around 1914¹⁶. The first plastic refractories were mixtures of plastic clay and crushed grog or calcined clay, supplied in a wet, mouldable (putty-like) form, installed chunk-by-chunk by workers using hammers. By the early 1930s pneumatic ramming devices were first recommended for the installation of plastics, the use of anchors for installing plastic refractory linings was in practice, and refractory concretes were applied using the 'cement gun'. Although Sainte-Claire Deville from France is considered the discoverer of the cementing properties of calcium aluminates, it was only in 1918 that the Lafarge Company in France commercially offered a calcium aluminate cement, produced from bauxite and lime. Around 1928 the commercial production of bagged mixes of refractory aggregates and calcium aluminate cement for monolithic refractory construction was started. By 1934 there were at least 25 of these proprietary mixes (called castables by the manufacturers) on the market. The first refractory concretes were simple mixtures of hydraulic cements and aggregates. By 1940 monolithic refractories only constituted 2–3% of the total refractory market, with products in the form of castables, plastic refractories and mortars. During the period 1940–1960 major breakthroughs were made in binders, with the introduction of intermediate and high-purity calcium aluminate cements (with CaO·Al₂O₃ as the principal anhydrous aluminate phase), and the development of phosphate bonding. The war years of 1941–1945 stimulated increased use of monolithic refractories due to their rapid rate of installation and therefore construction, which often removed the need for complete rebuilds. Graphitic plastics were first introduced in 1941. The first commercial phosphate-bonded plastic was introduced in the early 1950s, as were hot gunning repair. By 1960 castables based on

high-purity calcium aluminate cement and tabular alumina aggregates were fairly common, ramming mixes with Al₂O₃ contents exceeding 90% and useful at temperatures up to 1871°C were appearing, chrome ore-periclase ramming mixes were developed for the copper industry, graphitic and high-alumina plastics and ramming mixtures (air-setting and phosphate bonded) were commonly available. By 1960 monolithic materials constituted ~30% of the value of refractories in the US, and were competing with prefired refractories. The 1970s also saw the concept of steel fibre reinforcement for monolithic materials being introduced, and the development of vibratable plastic refractories. In the late 1970s low-cement castables were introduced in the US, and the gunning of conventional plastic refractories in the early 1980s. A major trend in monolithic material development from 1960–1984 was product specialization through innovative changes in raw material grain sizing, reduced binder contents through innovative uses of additives, and improved mixing and installation procedures⁸. From 1970–1980 monolithic materials, and mainly castables, proved their real value. By the early 1980s there were mouldings, ramming mixes, castables and precast shapes, gunning mixes, and newly developed vibration materials⁴³. The introduction of low-cement castables and cement-free castables were some of the most impressive developments during those years.

Castables

A significant development in monolithic technology was the development of refractory concretes or castables based on calcium alumina cements (CACs): from conventional castables (CaO>2.5%), to low cement castables (LCCs; 2.5%>CaO>1.0%), to ultra-low cement castables (ULCCs; 1.0%>CaO>0.2%) to cement-free castables (CaO<0.2%), the CaO content of the monolithic material is reduced, in order to improve its high temperature properties, through which the temperature at which it can be used is increased⁴⁴. Conventional castables require 8–15% water addition. The added water is taken up by the porosity of the grain, required for the hydraulic bond, and is required for the concrete to flow. Compared with brick that is based on the same raw materials, the concrete has the disadvantages of higher porosity, higher concentration of fluxes (CaO, Fe₂O₃), and low hot strength. The fluxes affect the corrosion resistance and hot strength negatively, while phase transformations associated with the dehydration process lead to a reduction in mechanical strength in the 538–982°C⁴⁵ temperature range. Castables with low cement contents, in which part of the cement content was replaced by fine particles (1–10 µm) or additives, were first referred to in a French patent in 1969⁴⁶. The crucial step was to use ultrafine particles ≤ 1 µm. These materials should be inert to hydration and should not form gels with water. The fine particles subsequently fill the voids between the coarse grains, which reduces water consumption, and therefore the porosity, and increases the strength of the material. Long drying periods are consequently required to avoid cracking and spalling⁸. Submicrometer powders commonly used in low cement (LC, containing 4–8% calcium alumina cement) and ultra-low cement (ULC, containing 1–2% calcium alumina cement) castables include microsilica (obtained from SiO₂-rich fume produced from the smelting of ferrosilicon and silicon metal,

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with an average particle diameter of ~15 mm) and Al_2O_3 ^{44,47}. Microsilica not only acts as a filler, but also reacts with the calcium aluminate phases in the cement and water to form zeolitic CASH phases. The chemically bonded water is subsequently not released abruptly, but progressively over a wide temperature range. One major problem still remained with low-cement castables: reaction between the reactive silica and calcium aluminate cement resulted in the formation of low-melting phases such as anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and gehlinit ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), as the CaO content in LCC varies between 1.0-2.5%⁸. The formation of viscous liquids at 1400°C and above contributes to the loss of strength of the castable. This can be avoided by replacing the microsilica with superfine Cr_2O_3 or superground calcined alumina, although the addition of chromium oxide is environmentally unacceptable in many countries. Conventional castables are installed by pouring, while flow and compaction of LCCs and ULCCs are usually promoted by internal or external vibration after pouring, since these materials are thixotropic in nature. Application of vibration can obviously cause problems as too little vibration causes lack of consolidation and compaction, while too much vibration causes segregation⁸. In an attempt to overcome the difficulties associated with vibration placement, a new class of LCCs and ULCCs was developed in the mid-1980s: the free or self-flowing castables (SFCs), which are sol-gel bonded castables or pumpables, have a modified rheology of the LCC and ULCC systems as a result of changing the shape and size distribution of the aggregates and a well-considered choice of deflocculants^{8,44}.

Colloidal silica is used as the main source in gel-bond technology⁸. The colloid is gelled around the refractory particles, and after drying forms a gel skeleton that provides strength to the refractory. The gel skeleton is highly reactive and forms mullite with fine alumina at relatively low temperatures. The gel-bond castables are more thermally stable and have higher thermal shock resistance, higher HMOR and refractoriness than cement-containing castables⁸. These are castables with a consistency after mixing that allows them to flow and degas without the application of external energy. The development of the SFCs led to the development of a new placement technique called wet

gunning or shotcreting (Figure 20). The first results on wet gunning of castables were published in 1963, but only in 1991 did it become an effective installation tool.

Other types of castables include insulating castables (which can be poured or gunned into position), conventional basic castables (which are mostly used for repair) as well as alumina-spinel and alumina-magnesia castables. The steel industry was also the driving industry for the development of alumina-spinel and alumina-magnesia castables⁴⁹. Spinel used in castables are either of stoichiometric composition or in the high alumina composition range, as magnesia-rich compositions create problems of hydration of the magnesia⁸. Spinel-reinforced or spinel-added castables (fine spinel grains added to the matrix), and spinel-forming castables (*in situ* formation due to reaction between added MgO and Al_2O_3)⁴ have gained popularity.

Gunning mixes

Gunning mixes can be installed quickly and are mostly used as a repair material⁸. Installation involves the transport of dry or semidry materials pneumatically by compressed air, with water addition at the nozzle (Figure 20). Gunning mixes can be lightweight for insulation or dense for more severe conditions, and can be used with different binders, depending on the application. These binders include clays, colloidal silica, dry phosphates, calcium alumina cements and organic compounds, such as molasses, lignosulphonates and synthetic resins.

Dry vibratables

Dry vibratables were developed during the late 1970s and early 1980s⁸. The significant advantage of a dry vibratable is that it can be used soon after being installed. Since dry vibratables contain no liquids, slow or prolonged heating is not required to avoid cracking or spalling. Dry mixes are placed in the dry state by either vibration or ramming⁷. Through their carefully designed particle size distribution they reach maximum compaction without the addition of liquids. The grain size distribution is therefore key in obtaining a dense and strong dry vibratable. The grains should be in close proximity to have the most effective solid-solid reaction. Small quantities of low-melting components form the initial bond at 400–600°C, while high-temperature ceramic bonding is achieved above 1200–1300°C. The formulation should therefore be such that the low-melting phases should react at high temperatures to form highly refractory phases. The dry vibratables may have a temporary bond (organic additives, sintering agents) but are eventually ceramically bonded through an increase in temperature⁷.

In situ refractories

The 1990s led to the use of refractory materials that are generated *in situ*, either within the refractory itself, or within the furnace, tank or kiln². The twentieth century has seen the use of slag freeze lines, water cooling and slag coatings in EAFs, slag splashing, clinker coatings in cement kilns, generation of a viscous layer in the glass adjacent to the AZS lining in glass tanks, a spinel bonding phase in magnesia-spinel brick in cement kilns and alumina-spinel CA castables for steel ladles as *in situ* refractories^{2,50}.

In situ refractories are defined as the in use product(s) of reaction within a refractory material or between the refractory

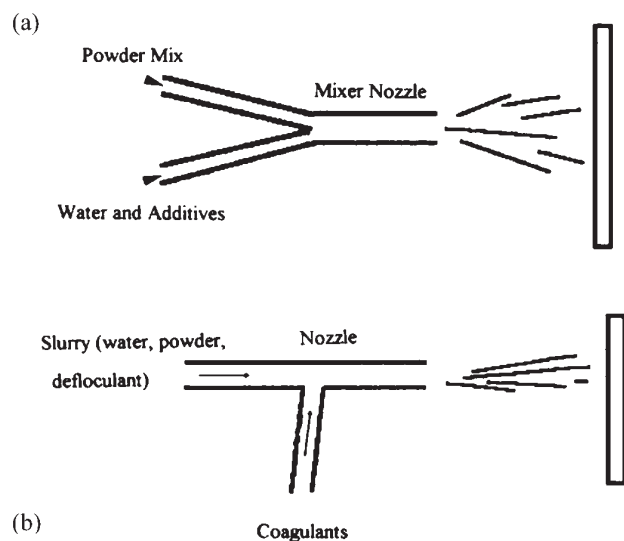


Figure 20—Difference between (a) gunning and (b) shotcreting⁴⁸

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material and furnace contents that lead to improved refractory behaviour⁵⁰. A distinction is made between four types of *in situ* refractory materials:

- ▶ **Type I:** The generation of useful phases throughout the matrix of the refractory material, e.g. spinel, forsterite and mullite.
- ▶ **Type II:** Reactions occur within the refractory material but are assisted by reaction with the liquid or vapour furnace contents, e.g. reactions of anti-oxidants (B₄C, Al, Si, Mg-Al alloys).
- ▶ **Type III:** A reaction occurs between the refractory and furnace contents whereby a protective layer is formed, e.g. clinker coatings in burning zones of cement kilns, viscous glass layers in contact with Al₂O₃-ZrO₂-SiO₂ blocks in glass tanks, a magnesio-wustite boundary layer between Fe-rich slag and MgO refractory.
- ▶ **Type IV:** Furnace contents are deposited onto the refractory, thus protecting the refractory material, e.g. slag splashing in BOF; freeze linings (copper coolers) in ilmenite, PGM, ferromanganese, silicomanganese and ferrochrome smelting applications.

Current developments

Environmental issues

Refractory materials can in general be considered to be 'energy-concentrated' materials (e.g. fusion-cast materials, production of high-fired bricks such as direct-bonded bricks). The trend towards the use of more monolithic materials and fewer high-fired bricks contributes to energy conservation in refractory production. However, the entire cycle, covering the production of the refractory material, as well as its application, must be considered, as highly energy-consuming refractory materials may be preferred if they save energy in their application⁵¹.

Refractory materials have, after removal from service, historically been landfilled. Change in the refractory industry has been driven strongly in terms of energy conservation and environmental protection⁵¹. Examples thereof include: reduction in energy consumption (development of binders that lead to high strength when refractories are fired at low temperatures⁵², the formation of spinel grain through mechanical alloying⁵³), reduction in emissions (e.g. change of air-fuelled firing technology to oxy-fuelled firing technology, whereby NO_x emissions are reduced⁴), development of non-toxic and environmentally friendly resins for carbon-containing refractory materials, and the replacement of coal tar pitches for impregnation by other benzo- α -pyrene (BaP) free carbonaceous agents⁵⁴.

Recycling is expected to become a key factor in saving energy and resources, protecting environments, addressing the raw materials shortage and soaring raw material prices in the industry⁵⁵. The recycling of spent refractory materials is considered to be a matter of survival that will enable the industry to achieve an environmentally and socially sustainable way of doing business⁵⁶.

Carbon-containing castables

Because LCCs and ULCCs consist of oxides, they suffer the same shortcomings as oxide-based refractory bricks, e.g. Al₂O₃-based castables have poor corrosion resistance (specifically in basic slag environments) and spalling resistance, and MgO-based castables have poor slag

penetration and spalling resistance. The improvement of the properties of oxide bricks through the addition of carbon suggested that graphite addition to oxide-based castables would improve properties. However, problems arose as graphite has poor aqueous wettability and dispersion, Al-based antioxidants have a tendency to hydrate¹¹, and they have lower strength after curing and drying⁵².

Research on C-containing castables for iron and steelmaking applications was initiated by CIREP (Centre for Industrial Refractories at École Polytechnique, Montréal) in 1996⁵⁷. The commercialization of carbon-containing castables has been hindered by poor water-wettability and dispersion ability of graphite, which result in castables that flow poorly, requiring a high water content for placement, which leads to high porosity after drying, and subsequent lowering of mechanical strength and corrosion resistance⁵⁸. To overcome these problems the use of surfactants or dispersants, micropellets of graphite and coating techniques concerning the graphite have been examined. The coatings can be oxides such as Al₂O₃, TiO₂, SiO₂, MgO, ZrO₂ or carbides such as SiC, TiC¹¹. Different techniques through which these coatings can be produced include mechanical impact treatment, sol-gel and molten salt synthesis. The main requirement is the formation of a uniform, crack-free, thick and strong bonded coating.

It was found that antioxidants play multifunctional roles in MgO-C castables: they protect carbon against oxidation, enhance hot strength, and play a role in the formation and deposition of secondary carbon, which improves slag-penetration resistance⁵⁹.

Trials have already been conducted in Brazil with a developed MgO-C self-flow castable for hot repairing of the BOF converter and steel ladle slag lines. This material is reported to be compatible with MgO-C bricks and basic steelmaking slags⁶⁰.

Nanotechnology

Nanotechnology aims to achieve enhanced material properties and functionality by dealing with matter on the atomic and molecular scale⁶¹. The first papers on nanotechnology and refractories that appeared during UNITECR 2003 created widespread interest^{62, 63}. These papers addressed the formation of a nanostructured matrix in MgO-C bricks. At UNITECR 2007 the papers on nanotechnology expanded to alumina-based refractory materials, ZrO₂-C materials and the production of nanosized MgAl₂O₄ particles.

A variety of nanoscale materials are already used or have the potential to be used in refractory products. These include nanoscale carbon black (pure elemental carbon in the form of nanoscale particles with a semi-amorphous molecular structure), carbon nanotubes (long seamless cylinders of one-atom-thick layers of graphite with diameters of a few nanometres), metallic nanoscale materials (for use as anti-oxidants), colloidal (nanoscale) silica (which has been used in the refractories industry for many years) whereby a nanostructured matrix is produced⁶¹. Technology also exists for the production of almost any oxide, such as MgO, Al₂O₃, ZrO₂, Cr₂O₃ and spinel, on nanoscale^{53, 64}. Huizhong *et al.* have shown that by adding nano-sized alumina and silica into a corundum-based refractory mixture the calcining temperature can be lowered by 100 to 200°C, while enhancing the CMOR and CCS⁶⁵. The Japanese have already commercialized refractories in which nanotechnology is

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applied: The development of nanographitized black containing MgO-C bricks means that lower levels of carbon can be used in these bricks with a reduction in the modulus of elasticity, improved thermal shock resistance, excellent corrosion resistance and good oxidation resistance⁶⁶.

The use of highly reactive nanoparticles open up a vast range of possibilities as sintering agents and participants in matrix phase formation through *in situ* reactions. Problems associated with these nanoscale materials are related to their cost, availability, handling, dispersion and mixing, as well as health and safety aspects associated with the handling of these very fine materials.

MgAl₂O₄-containing refractories

Due to their high refractoriness, mechanical strength, thermal shock and corrosion resistance MA (MgAl₂O₄), spinel-containing refractories are increasingly finding new applications, and new types of spinel-containing refractories are being developed. It is anticipated that continuous improvement in their synthesis techniques will take place, but novel techniques such as mechanochemical alloying and molten salt synthesis may become significant methods whereby high quality spinels can be produced at lower temperatures and cost³⁷.

An extensive research effort on Al₂O₃-MgO-based castables and bricks is currently also driven by FIRE (The Federation for International Refractory Research and Education)⁶⁷.

R&D

The internationalization of ownership of refractories producers has resulted in centralization of research as well as heightened concern for standards and the availability of independent test facilities². South Africa has, apart from its dependence on other countries for refractory raw materials, become part of the global village through this internationalization of ownership. The South African refractories industry therefore shares the same concerns.

It is foreseen that, due to much reduced R&D activity, as well as registered patents (Figure 21), cost restraints and difficulty with experimentation, there will be an increased focus on thermomechanical and thermodynamic modelling²,⁶⁸. It is also predicted that future studies on slag attack of refractory materials will involve high-temperature *in situ* characterization of corrosion mechanisms (e.g. X-ray transmission, neutron reflexion spectroscopy and nuclear magnetic resonance).

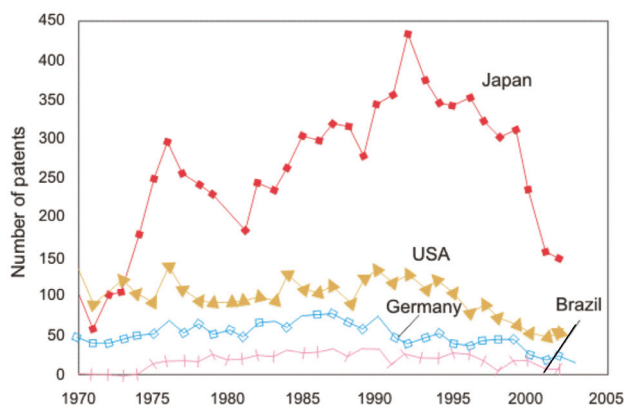


Figure 21—Registered patents in refractory materials in Japan, 1970–2003¹³

The founding and activities of FIRE also promise to have a pronounced influence on R&D in refractory materials. FIRE is a network of seven academic institutions (Montanuniversität Leoben—Austria; Universidade Federal de São Carlos—Brazil; ENSCI—Limoges, France; Polytech'Orléans—Orleans, France; Technische Universität Bergakademie Freiberg—Germany; Nagoya Institute of Technology—Japan; University of Missouri-Rolla—Rolla, US), sponsored by nine partners from industry (RHI-AG, Magnesita SA, Pyrotek Inc, Almatis, inc., Kerneos, Corus Ceramics Research Centre, Alcan Bauxite and Alumina, Alcoa, inc., ANH Refractories, Vale-INCO and Calderys), which promote research and education in refractory engineering⁶⁹. Their main objectives are to fund international studies and research activities in the field of refractories, to support academic education by encouraging student exchanges and generating joint degree programmes, and to combine the expertise, experience and passion of competent persons, institutions and companies in the field of refractory materials.

The concept of FIRE was presented in November 2003 at UNITECR'03, in Osaka, while the first academic programmes started in 2006–2007. The current FIRE research programmes are based on thermomechanical behaviour of refractories, modelling and testing, design of cement-bonded refractories (Al₂O₃-MgO castables), thermochemical behaviour of refractories modelling and corrosion testing (Al₂O₃-MgO castables/bricks)⁶⁷.

Conclusions

The refractories industry has developed from a trial-and-error approach, using mainly natural materials, into a highly innovative industry, which uses composite oxide-carbon-metal systems, based on *in situ* technologies and innovative application methods. It has grown in response to developments in particularly the iron and steel industry. The driving force for change has been improved process technology and a desire for higher productivity via longer campaign lives, but increasingly also better use of energy, the need to protect the environment, as well as the reduction, reuse and recycling of refractory waste materials²,⁶¹.

The field of refractory materials has become very broad, and the technology increasingly sophisticated. The evolutionary process is far from complete, and will develop further through the continuous interchange of ideas between the research teams of refractory manufacturers, the users of refractory materials, and the contribution from researchers at academic institutions.

The design and technological principles behind refractory materials are indeed very 'cool', and future prospects are that these materials will become even cooler in the foreseeable future!

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