*Kirk-Othmer Encyclopedia of Chemical Technology.*

# REFRACTORIES

Refractories are materials that resist the action of hot environments by containing heat energy and hot or molten materials (1). There is no well-established line of demarcation between those materials that are and those that are not refractory. The ability to withstand temperatures above 1100°C without softening has, however, been cited as a practical requirement of industrial refractory materials (see Ceramics). The type of refractories used in any particular application depends on the critical requirements of the process. For example, processes that demand resistance to gaseous or liquid corrosion require low permeability, high physical strength, and abrasion resistance. Conditions that demand low thermal conductivity may require entirely different refractories. Combinations of several refractories are generally employed.

## 1. Physical Forms

Refractories may be preformed, ie, shaped, or formed and installed on-site, ie, specialties. Innovations in placement and vessel construction has led to a greater emphasis on specialty refractory products. Castables, gunning mixes, and plastic and ramming mixes are used either for repair or for complete new construction of what is known as monolithic linings. The tendency to use monolithics instead of constructions using shaped products has been steadily increasing. As of the mid-1990s, monolithic installations are as common as conventional shaped product construction.

### 1.1. Brick

The standard dimensions of a refractory brick are 229 mm (9 in.) length, 114 mm (4.5 in.) width, and 64 mm (2.5 in.) thickness. This is known as a standard straight. Quantities of bricks are given in brick equivalents, that is, the number of standard straight bricks that have a volume equal to that of the particular installation. The actual shape and size of bricks depends on the design of the vessel or structure in question and may vary considerably from the standard straight brick. For example, bricks for basic oxygen furnaces (BOF), also called BOP or LD vessels, may be in the shape of a key 660 mm long, 76 mm thick, and tapering in width from 152 to 102 mm. Numerous other shapes are available from manufacturers as standard items as well as custom-made or special ordered shapes.

Bricks may be extruded or dry-pressed on mechanical or hydraulic presses. Formed shapes may be burned before use, or in the case of pitch or resin/chemically bonded bricks, may be cured (tempered) at a low temperature.

### 1.2. Setter Tile and Kiln Furniture

These products are formed in a similar manner to bricks and are used to support ware during firing operation. The wide variety of available shapes and sizes include flat plates, posts, saggers, and car-top blocks.

### 1.3. Fusion-Cast Shapes

Refractory compositions are arc-melted and cast into shapes, eg, glass-tank flux blocks as large as $305 \times 610 \times 1219$ mm. After casting and annealing, the blocks are accurately diamond ground to ensure a precise fit.

### 1.4. Cast and Hand-Molded Refractories

Large shapes such as burner blocks and flux blocks, and intricate shapes such as glass feeder parts saggers are produced by casting slips, hydraulic cement bonded mixtures, or hand-molding clay or chemically bonded materials. Because these techniques are labor intensive, they are reserved for articles that cannot be satisfactorily formed in any other way, owing to complexity or small production quantities.

### 1.5. Insulating Refractories

Insulating refractories in the form of brick are much lighter than conventional bricks of the same composition by virtue of the brick porosity. The porosity may be introduced by means of lightweight grog or additives that create porosity by a foaming action or by evolution of combustion or decomposition products during the burning process. Refractory fibers (qv) made from molten oxides may be formed into bulk fiber, blankets, boards, or blocks. Such fiber products are used as back-up thermal insulation and low heat-capacity linings in kilns and reheat furnaces (see Insulation, Thermal).

### 1.6. Castables and Gunning Mixes

Castables consist of refractory grains to which binders are added. Upon mixing with water, the bond reacts and binds the mass together. Usually this binder is a hydraulic refractory cement. Low (5%) cement, ultralow ($<3\%$) cement, and no-cement castables have been introduced. These castables usually contain chemical deflocculants, dispersants, retarders, and very fine batch ingredients such as silica fume or fine alumina. The products usually contain low water additions. Castables may be placed by vibration, pumping, and in some cases can be made to self-flow (self-leveling castables). The impetus to reduce the cement content in castables has been the desire to improve performance by reducing the low melting eutectics in the lime–alumina–iron–silica system. This has been a principal thrust in refractory development since the mid-1980s.

Gunning mixes are designed to be conveyed pneumatically through a nozzle under water and air pressure. The mixture may be slurried before being shot through the gun or mixed with water at the nozzle. In addition to refractory grains, the mix may contain clay and nonclay additives to promote adherence to the furnace wall. Gunning mixes may be made from cement-bonded refractories, usually based on alumina or aluminosilicate materials, or from basic raw materials which are bonded with silicate or phosphate bonds. The advantage of gunning results from the ability to form large sections quickly without the need for forms. In the case of basic gunning mixes, repairs can be made without removing the furnace from service. That is, the gunning repair can be carried out on hot vessel walls.

### 1.7. Plastic Refractories and Ramming Mixes

Plastic refractories are mixtures of refractory grains and plastic clays or plasticizers with water. Ramming mixes may or may not contain clay and are generally used with forms or steel work. The amount of water used in these products varies but is held to a minimum to facilitate drying. Plastics are generally supplied in a ready-to-use state.

### 1.8. Mortars

Mortars consist of finely ground refractory grains and plasticizers so that a thin coating on the brick can be obtained by dipping. The mortar must be chemically compatible with the refractory lining. This compatibility is established by principles of phase equilibria. The mortars may be designed to bond with the refractories by high temperature reactions during sintering or chemical bonds resulting from additions of sodium silicate, phosphates, cement, or colloidal particles. The conditions needed to cure these chemical bonds range from exposure to air to low temperature heat treatments. Sometimes the heat treatment required to set the bond occurs during the normal furnace or vessel operation, obviating the need for a separate curing procedure.

### 1.9. Composite Refractories

Although many refractories may be considered composites, examples of composites analogous to metal and organic composites are not common (see Composite materials). Shaped and specialty refractories containing metallic reinforcements have appeared on the market. Additives such as flake graphite and active metals such as silicon, aluminum, magnesium, and alloys, have been used for nonwetting characteristics and as antioxidants for carbon-containing refractories, respectively.

### 1.10. Refractory Coatings

Refractory coatings (qv) may be applied in a variety of ways. Painting or spraying a fine-grained refractory mix at room temperature yields a dense sintered coating upon heating. Other techniques include thermal or plasma spraying, and chemical vapor deposition. In the first, the powdered coating material is fed into a burner and sprayed at elevated temperatures. The pyroplastic grains form a dense monolithic coating when they impinge on the substrate. Plasma spraying is carried out in essentially the same manner, except that an electrically ionized gas plasma heats the coating powder to temperatures up to 16,700°C.

## 2. Raw Materials

In the past, refractory raw materials were used essentially as mined minerals (2–7). Selective mining yielded materials of the desired properties and only in cases of expensive raw materials, such as magnesite, was a beneficiation process required. As of this writing (ca 1995), high purity natural raw materials are increasingly in demand as is synthetically prepared refractory grain made from combinations of high purity and beneficiated raw materials (Tables 1 and 2). The material produced upon firing raw as-mined minerals or synthetic blends is called grain, clinker, co-clinker, or grog. Recycled materials produced by the manufacturers and recovered from users are also being increasingly used to reduce waste. Use of recycled materials has been found to improve refractory performance in some cases when proper care over handling (reclamation) has been exercised. Use of recycled materials is limited in the United States. It is a bit more common in Europe and is expected to increase (see Recycling).

**Table 1. Composition of Refractory Raw Materials, %[a, b]**

| Name | Location | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | MgO | Alkalies |
|---|---|---|---|---|---|---|---|---|
| | | Silica raw materials | | | | | | |
| ganister | Bwlehgwyn (N. Wales, U.K.) | 97.4 | 0.73 | 0.78 | 0.1 | | | |
| gravel | Sharon Conglomerate, Ohio | 98.0 | 0.3 | 0.5 | 0.1 | | | |
| | | Clays | | | | | | |
| flint clays | Pennsylvania | 50.40 | 34.58 | 1.42 | 2.06 | 0.45 | 1.00 | 1.58 |
| | Missouri | 43.80 | 38.29 | 0.60 | 2.33 | 0.07 | 0.20 | 0.39 |

**Table 1. *Continued***

| Name | Location | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | MgO | Alkalies |
|---|---|---|---|---|---|---|---|---|
| | Kentucky | 44.94 | 35.17 | 1.56 | 3.12 | 0.11 | 0.18 | 1.45 |
| | People's Republic of China | 51.20 | 46.62 | 0.87 | 0.87 | | | 0.15 |
| plastic clays | Pennsylvania | 54.00 | 27.94 | 1.39 | 2.45 | 0.07 | 1.22 | 3.33 |
| | Missouri | 55.12 | 28.65 | 1.66 | 1.55 | 0.11 | 0.10 | 2.54 |
| | Kentucky | 56.42 | 26.92 | 2.05 | 1.95 | 0.18 | 0.51 | 1.75 |
| kaolin | Georgia | 43.00 | 37.55 | 0.85 | 2.10 | 0.09 | 0.18 | 0.15 |
| | Florida | 46.5 | 37.62 | 0.51 | 0.36 | 0.25 | 0.16 | 0.42 |
| fireclay | Stourbridge (Scotland) | 68.1 | 27.2 | 1.95 | 1.1 | 0.72 | 0.35 | 1.28 |
| | Pfalz (Germany) | 45.1 | 36.3 | 2.21 | 1.12 | 0.08 | 0.11 | 2.25 |
| plastic | Chasov-Yar (Russia) | 51.6 | 33.3 | 0.9 | 1.37 | 0.53 | 0.57 | 3.28 |
| semikaolin | Suvorov (Russia) | 46.1 | 33.9 | 2.14 | 1.52 | 0.41 | 0.23 | 0.44 |
| kaolin | Vladimirovka (Russia) | 48.3 | 36.7 | 0.83 | 0.78 | 0.3 | 0.33 | 0.77 |
| High alumina | | | | | | | | |
| natural | | | | | | | | |
| siliceous bauxite[c] | | | | | | | | |
| ca 70% $Al_2O_3$ | Eufaula, Alabama | 25.9 | 70.1 | 1.13 | 2.9 | 0.05 | 0.03 | 0.13 |
| ca 60% $Al_2O_3$ | Eufaula, Alabama | 34.9 | 60.6 | 1.26 | 2.5 | 0.07 | 0.12 | 0.11 |
| | People's Republic of China | 32.40 | 63.50 | 1.50 | 2.20 | | | 0.20 |
| ca 50% $Al_2O_3$ | People's Republic of China | 43.30 | 52.80 | 1.42 | 1.90 | | | 0.19 |
| South American bauxite[c] | Guyana | 7.0 | 87.5 | 2.00 | 3.25 | trace | trace | trace |
| Chinese bauxite[c] | People's Republic of China | 6.0 | 87.5 | 1.50 | 3.75 | | | 0.50 |
| kyanite[d] | Virginia | 38.6 | 59–61 | 0.2–0.9 | 0.67 | 0.03 | 0.01 | 0.4 |
| sillimanite[d] | India | | 59–61 | | | | | |
| synthetic | | | | | | | | |
| fused alumina | | | | | | | | |
| black | | 0.48 | 97.3 | 0.15 | 2.45 | 0.07 | 0.11 | 0.05 |
| gray | | 0.06 | 99.5+ | 0.15 | 0.06 | trace | trace | 0.07 |
| sintered alumina | | 0.06 | 99.5 | 0.06 | trace | trace | trace | 0.05 |
| sintered mullite | Georgia | 27.90 | 68.00 | 1.33 | 2.61 | 0.06 | 0.04 | 0.06 |
| sintered magnesiumaluminate | Japan | 0.2 | 67.90 | 0.2 | | 0.3 | 31.9 | |
| fused mullite | | 22.0 | 77.7 | 0.12 | 0.05 | trace | trace | 0.35 |
| calcium aluminate cement | | | | | | | | |
| low purity | | 8.4 | 42.0 | 10.7 | | 37.0 | 1.2 | |
| high purity | | 0.1 | 79.0 | 0.3 | trace | 18.0 | 0.1 | 0.5 |
| Zirconium | | | | | | | | |
| zircon[e] | | 32.5 | 0.08 | 0.05 | 0.06 | trace | trace | trace |
| baddeleyite[f] | Brazil | | | 3–5 | | | | |
| Basic raw materials | | | | | | | | |
| calcined magnesias | | | | | | | | |
| natural magnesite | Austria | 0.3 | 0.3 | 5.4 | | 2.7 | 91.3 | |
| | Greece | 1.2 | 0.3 | 0.3 | | 2.8 | 95.4 | |
| | U.S. | 1.00 | 0.36 | 0.65 | | 3.02 | 94.97 | |
| | People's Republic of China | 0.40 | 0.13 | 1.73 | | 1.31 | 96.36 | |
| | Turkey | 1.42 | <0.02 | <0.02 | | 1.58 | 96.95 | |
| seawater | Japan | 0.37 | 0.04 | 0.01 | | 1.23 | 98.32 | |
| | U.K. | 0.70 | 0.20 | 0.10 | | 2.30 | 96.66 | |
| | U.S. | 0.80 | 0.12 | 0.14 | | 2.22 | 96.70 | |
| | U.S | 0.80 | 0.15 | 0.22 | | 2.65 | 96.12 | |
| | Ireland | 0.83 | 0.18 | 0.17 | | 1.07 | 97.75 | |
| brine | Israel | 0.14 | 0.02 | 0.04 | | 0.77 | 99.45 | |
| dolomite | U.K. | 1.8 | 1.1 | 5.9 | | 54.6 | 36.4 | |
| dolomite, low flux | U.S. | 0.7 | 0.3 | 0.9 | | 57.7 | 40.4 | |
| chrome ore[g] | Africa | 3.8 | 14.9 | 27.1 | | 0.3 | 9.9 | |

**Table 1. *Continued***

| Name | Location | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | MgO | Alkalies |
|---|---|---|---|---|---|---|---|---|
|  | Philippines | 5.5 | 31.0 | 15.5 |  | 0.5 | 16.0 |  |

[a] Refs. 2 and 5.

[b] Difference between total analysis and 100 = loss on ignition, %.

[c] Calcined.

[d] Raw.

[e] Contains a trace of $Cr_2O_3$ and 66.7% $ZrO_2$.

[f] Contains 70.8% $ZrO_2$.

[g] African chrome ore contains 44.0% $Cr_2O_3$; Philippine, 31.5%.

### 2.1. Silica

The most common refractory raw materials are ganister, which is a dense quartzite, and silica gravels (see Silica; Silicon compounds). The latter are generally purer than the former and are often further beneficiated by washing to give the raw material for superduty silica brick having no more than 0.5% impurities (alkalies, $Al_2O_3$, and $TiO_2$). Quartzite and gravel deposits are widespread throughout the world. The most important U.S. deposits are found in Pennsylvania, Ohio, Wisconsin, Alabama, Colorado, and Illinois. Synthetically produced electrofused silica is a thermally stable, shock-resistant, high purity raw material.

**Table 2. Physical Properties of Refractory Raw Materials[a]**

|  |  |  | Specific gravity, g/cm$^3$ |  |  |
|---|---|---|---|---|---|
| Material | Pyrometer cone equivalent | Main crystalline phases | Bulk | True | Apparent porosity, % |
|  |  | Silica |  |  |  |
| ganister |  | quartz |  | 2.66 | 1.6 |
| gravel |  | quartz |  | 2.61 | 0.3 |
|  |  | Clays |  |  |  |
| flint clays | 32–33 |  |  |  |  |
|  | 34 | kaolinite, illite, quartz |  |  |  |
|  | 33 | kaolinite, quartz, illite | 2.55 |  |  |
| plastic clays | 31 | kaolinite, quartz, illite |  |  |  |
|  | 30 | kaolinite, quartz, illite |  |  |  |
|  | 30 | kaolinite, quartz, illite |  |  |  |
| kaolin | 33–34 | kaolinite |  |  |  |
| fireclay | 33–34 | kaolinite |  |  |  |
| plastic | 32–33 | kaolinite, illite |  |  |  |
| semikaolin | 32–33 |  |  |  |  |
| kaolin | 32–33 |  |  |  |  |
|  |  | High alumina |  |  |  |
| natural siliceous bauxite[b] |  |  |  |  |  |
| ca 70% $Al_2O_3$ | 38–39 | mullite | 2.85–2.95 | 3.1–3.2 | 4–8 |
| ca 60% $Al_2O_3$ |  | mullite | 2.75–2.85[c] | 2.95–3.05 | 3–7 |
| ca 50% $Al_2O_3$ |  |  | 2.65 |  |  |
| South American bauxite[b] |  | corundum, mullite | 3.1 | 3.6–3.7 | 15–20 |
| Chinese bauxite[b] |  |  | 3.20 |  |  |
| kyanite[d] | 36–37 | kyanite |  | 3.5–3.7 |  |
| sillimanite[d] |  | sillimanite |  | 3.23 |  |
| synthetic |  |  |  |  |  |
| fused alumina |  |  |  |  |  |
| black | 42 | $\alpha$-alumina | 3.87 | 4.01 | 3.49 |

**Table 2. *Continued***

| | | | Specific gravity, g/cm$^3$ | | |
|---|---|---|---|---|---|
| Material | Pyrometer cone equiva-lent | Main crystalline phases | Bulk | True | Apparent porosity, % |
| gray | 42+ | $\alpha$-alumina | 3.95 | 3.98 | 0.5–1.0 |
| sintered alumina | 42+ | $\alpha$-alumina | 3.45–3.6 | 3.65–3.80 | 5.0 |
| sintered mullite | 39 | | 2.85 | | |
| sintered magnesium aluminate | | spinel, periclase | 3.33 | | |
| fused mullite | 39 | mullite | 3.1 | 3.45 | 0.1 |
| calcium aluminate cement | | | | | |
| low purity | | calcium monoaluminate | | | |
| high purity | 34 | $\alpha$-alumina, calcium monoaluminate | | | |
| | | Zirconium | | | |
| zircon | | zircon | | 4.2–4.6 | |
| baddeleyite, $ZrO_2$ | | baddeleyite | | 5.5–6.5 | |
| | | Basic raw materials | | | |
| calcined magnesias | | | | | |
| natural magnesite | | periclase | 3.2 | | |
| | | periclase | 3.4 | | |
| | | magnesite, dolomite, calcite | 3.40 | | |
| | | [e] | 3.39 | | |
| seawater | | periclase | 3.44 | | |
| | | periclase | 3.35 | | |
| | | periclase | 3.40 | | |
| | | periclase | 3.22 | | |
| brine | | periclase | 3.41 | | |
| dolomite[f] | | periclase + CaO | | | |
| | | periclase + CaO | | | |
| chrome ore | | chromite spinel | 4.2 | | |
| | | chromite spinel | 3.9 | | |

[a] Refs. 2 and 5.

[b] Calcined.

[c] Another type of ca 60% $Al_2O_3$ natural siliceous bauxite has a bulk density of 2.70 g/cm$^3$.

[d] Raw.

[e] Unclassified.

[f] Both regular and low flux dolomite.

### 2.2. Fireclay

Fireclays consist mainly of the mineral kaolinite [1318-74-7], $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$, with small amounts of other clay minerals, quartzite, iron oxide, titania, and alkali impurities. Clays (qv) can be used in the raw state or after being calcined. Raw clays may be coarsely sized or finely ground for incorporation in a refractory mix. Some high purity kaolins like those that occur in Georgia are slurried, classified, dried, and air-floated to achieve a consistent high quality. The classified clays (qv) also may be blended and extruded or pelletized, and then calcined to produce burned synthetic kaolinitic grog, or coarsely crushed raw kaolinite may be burned to produce grog. Upon calcination or burning, kaolinite decomposes to mullite and a siliceous glass incorporating mineral impurities associated with the clay deposit, eg, quartzite, iron oxide, titania, and alkalies, and is consolidated into dense hard granular grog at high temperatures. Fireclay deposits are widely distributed; in the United States they occur in Pennsylvania, Missouri, and Kentucky.

#### *2.2.1. Bauxitic Kaolins and Mullites*

Deposits of bauxitic kaolins, kaolins having aluminous minerals, have been discovered that have alumina contents between 50 and 70%. These materials are made into refractory aggregates called calcines, grog, clinker, or grain. In addition to selectively mined deposits, synthetic compositions can be prepared from kaolin and alumina and other minerals to produce compositions of desired alumina and mineralogical content. These synthetic mullites are readily available in the form of sintered and fused aggregates.

### 2.3. High Alumina

The naturally occurring raw materials are bauxites, sillimanite [12141-45-6] group minerals, and diaspore clays (see Aluminum compounds). Other high alumina raw materials are made by beneficiation, blending, and other processing techniques.

### 2.4. Bauxites

Bauxite [1318-16-7] consists mainly of gibbsite [14762-49-3], $Al(OH)_3$, and varying amounts of kaolinite, and iron and titania impurities. Because the loss on ignition is high, bauxite must be calcined to high temperatures before use. During calcination, it is converted to a dense grain consisting mainly of corundum [12252-63-0], $Al_2O_3$, and mullite. Refractory-grade bauxite is relatively rare because a high iron content makes most bauxites unsuitable for refractory use. Commercially mined deposits are in South America, especially Guyana and Surinam, and the People's Republic of China. Other deposits occur in India and Central Africa but are not mined for refractory grades at present.

### 2.5. Sillimanite Minerals

This group includes sillimanite, andalusite [12183-80-1], and kyanite [1302-76-7]. All have the formula $Al_2O_3{\cdot}SiO_2$. Upon heating, a mixture of mullite, silica, and a siliceous glass is obtained. The specific gravity of sillimanite and andalusite is ca 3.2, and that of kyanite is 3.5. Thus, kyanite expands upon conversion to mullite by ca 16–18 vol %, but sillimanite and andalusite expand only slightly. Kyanite is found in India and South Africa, and in the United States in Virginia and South Carolina. Large-grained kyanite is rare, and the largest size commercially available from U.S. sources is ca 500 $\mu$m (35 mesh). Refractory-grade sillimanite occurs in India and South Africa.

### 2.6. Mullite

Although mullite is found in nature, for example, as inclusions in lava deposits on the island of Mull, Scotland, no commercial natural deposits are known. It is made by burning pure sillimanite minerals or sillimanite–alumina mixtures. Fused mullite of high purity is obtained by arc-melting silica sand and calcined alumina. High purity sintered mullite is made from alumina and silica, but requires mineralizing agents and very high temperatures.

### 2.7. Alumina

A pure although not necessarily a refractory grade of alumina is obtained from bauxite by the Bayer process. In this process, the gibbsite from the bauxite is dissolved in a caustic soda solution and thus separated from the impurities. Alumina, calcined, sintered, or fused, is a stable and extremely versatile material used for a variety of heavy industrial, electronic, and technical applications.

Calcined alumina is a reactive powder used to make synthetic grain. It also may be used as a bonding or fine component in batched refractory mixes, as a raw material for molten cast refractories, or for refractory casting slips.

Sintered alumina, also known as tabular alumina, is formed by burning aggregates made from reactive calcined alumina to high temperatures to obtain a stable high purity corundum grain. Fused alumina is obtained by fusing either calcined alumina or bauxite. Bauxite is beneficiated during fusion as iron and silica are removed as ferrosilicon. A special grade of fused alumina is obtained by blowing air through a stream of molten alumina. These hollow spheres of alumina, called bubble alumina, make an excellent medium weight aggregate of high purity and refractoriness (see Aluminum compounds).

### 2.8. Calcium Aluminate Cements

Low purity calcium aluminate [12042-78-3] cements are obtained by sintering or fusing bauxite and lime in a rotary or shaft kiln. A high purity calcium aluminate cement, $2CaO{\cdot}5Al_2O_3$, capable of withstanding service temperatures of 1750°C can be prepared by the reaction of high purity lime with calcined or hydrated alumina (see Aluminum compounds).

### 2.9. Zirconia

Zircon (zirconium silicate), the most widely occurring zirconium-bearing mineral, is dispersed in various igneous rocks and in zircon sands. The main deposits are in New South Wales, Australia; Travancore, India; and Florida in the United States. Zircon can be used as such in zircon refractories or as a raw material to produce zirconia. The zircon structure becomes unstable after about 1650°C, depending on its purity, and decomposes into $ZrO_2$ and $SiO_2$ rather than melting (see Zirconium and zirconium compounds).

Zirconia occurs as the mineral baddeleyite [12036-23-6], for instance, in a deposit around Sao Paulo, Brazil. However, these baddeleyite deposits generally contain large amounts of impurities and only about 80% $ZrO_2$. High purity zirconia can be obtained from baddeleyite by leaching with concentrated sulfuric acid or chlorination at high temperatures. The zirconium sulfates and chlorides thus formed are readily separated from the impurities. Zirconia also is made from zircon by electric-arc melting under reducing conditions. Here, the silica is separated from the zirconia by adding iron to form ferrosilicon. The most remarkable property of zirconia is its volume instability. Upon heating, unstabilized $ZrO_2$ transforms from the low temperature monoclinic form to the tetragonal form at about 1000°C, resulting in a 9% volume contraction. By adding impurities such as magnesia, calcia, or yttria, zirconia can be transformed into a cubic crystal phase stable at all temperatures, although often only enough impurities are added for partial stabilization, ie, both cubic and either the tetragonal or monoclinic forms exist.

### 2.10. Basic Raw Materials

#### *2.10.1. Magnesite*

Calcined or dead-burned magnesite [13717-00-5] is obtained by firing naturally occurring magnesium carbonate to 1540–2000°C. This treatment produces a dense product composed primarily of periclase [1309-48-4], MgO. Large sedimentary deposits of magnesite occur in Austria, Manchuria, Greece, the Ural Mountains, and in the United States in Washington, Nevada, and California. Calcia, silica, alumina, and iron-bearing phases occur as accessory minerals (see Magnesium compounds).

Synthetic magnesia is most often produced from seawater, known as seawater magnesia. Seawater contains approximately 1294 ppm Mg. Synthetic magnesia can also be produced from brine wells or lakes which have much higher concentrations of magnesium. Regardless of the source of magnesium, the sea or brine water is treated with hydrated lime, $Ca(OH)_2$, that precipitates $Mg(OH)_2$:

$$Ca\,(OH)_2 + MgCl_2\ \ (aq) \longrightarrow Mg\,(OH)_2 + CaCl_2$$

The $Mg(OH)_2$ precipitate is filtered, dried, and calcined to produce caustic magnesia. The caustic magnesia is then mechanically compacted and sintered to form a dense granular product. Large seawater or brine plants are located in the United States (Gulf of Mexico, California, Michigan, and New Jersey), Mexico, the United Kingdom, Ireland, Israel, Italy, Japan, and Russia. Magnesium hydroxide also occurs in sedimentary deposits as the mineral brucite [1317-43-7], eg, in Quebec and Nevada.

### *2.10.2. Dolomite*

Dolomite [17069-72-6], $CaMg(CO_3)_2$, occurs in widespread deposits in many areas including southern Austria, the U.K., Russia, and the United States. Raw dolomite may be used for certain refractories, but in most instances it is calcined to form a grain consisting primarily of MgO (periclase) and CaO [1305-78-8]. Calcined dolomite absorbs $H_2O$ and $CO_2$ from the atmosphere and eventually disintegrates. Fluxes such as $SiO_2$, $Fe_2O_3$, and $Al_2O_3$ increase hydration resistance but also sharply reduce the fusion point of the dolomite. High purity, low flux dolomites with less than 2% impurities are produced by high temperature calcination of natural dolomites in Ohio and Pennsylvania (see Lime and limestone).

### *2.10.3. Forsterite*

Pure forsterite is rare in nature. Most natural magnesium orthosilicates form solid solutions of fayalite, $Fe_2SiO_4$, and forsterite. Forsterite refractories are usually made by calcining magnesium silicate rock such as dunite, serpentine, or olivine with sufficient magnesia added to convert all excess silica to forsterite and all sesquioxides to magnesia spinels.

### *2.10.4. Chrome Ore*

Chromia-bearing spinel materials, although considered neutral, are generally used in combination with basic magnesite. Chrome ores consist essentially of a complex solid-solution series of spinels including hercynite, $FeO{\cdot}Al_2O_3$; ferrous chromite, $FeO{\cdot}Cr_2O$; magnesioferrite, $MgO{\cdot}Fe_2O_3$; picrochromite, $MgO{\cdot}Cr_2O_3$; spinel, $MgO{\cdot}Al_2O_3$; and magnetite, $FeO{\cdot}Fe_2O_3$. Silicate phases such as serpentine, talc (qv), and enstatite are commonly associated with the spinel grains. The principal deposits of chrome ore occur in Africa (Transvaal, South Africa, Zimbabwe), Russia, Turkey, Greece, Cuba, and the Philippines; African and Russian chrome ores are high in iron content, and Cuban and Philippine ores are higher in alumina.

### *2.10.5. Silicon Carbide*

Silicon carbide is made by the electrofusion of silica sand and carbon. Silicon carbide is hard, abrasion resistant, and has a high thermal conductivity. It is relatively stable but has a tendency to oxidize above 1400°C. The silica thus formed affords some protection against further oxidation (see Carbides).

### *2.10.6. Beryllia and Thoria*

These are specialty oxides for highly specialized applications that require electrical resistance and high thermal conductivity. Beryllia is highly toxic and must be used with care. Both are very expensive and are used only in small quantities.

### *2.10.7. Carbon and Graphite*

Carbon (qv) and graphite [7782-42-5] have been used alone to make refractory products for the lower blast furnace linings, and electrodes for steel and aluminum production. They are also commonly used in conjunction with other refractory raw materials. These materials are highly refractory nonwettable materials and are useful refractories in nonoxidizing environments. Carbon blacks are commercially manufactured, whereas graphite for refractory use has to be mined.

## 3. General Properties

### 3.1. Oxides

A number of simple and mixed refractory oxide materials are described in Table 3. The most widely used simple oxide is $Al_2O_3$. It has moderate thermal shock resistance, good stability over a wide variety of atmospheres, and is a good electric insulator at high temperatures. The strength of ceramics is influenced by minor impurities and microstructural features. In general, polycrystalline alumina has reasonably good and nearly constant strength up to about 1000–1100°C; at higher temperatures, the strength drops to much less than one-half of the room temperature value over a 400°C temperature increment. Single-crystal alumina is stronger than polycrystalline $Al_2O_3$ and actually increases in strength between 1000 and 1100°C. Fused silica glass has excellent thermal shock properties but devitrifies on long heating above 1100°C and loses much of its shock resistance.

Beryllium and magnesium oxides are stable to very high temperatures in oxidizing environments. Above 1700°C MgO is highly volatile under reducing conditions and in vacuum, whereas BeO exhibits better resistance to volatilization but is readily volatilized by water vapor above 1650°C. Beryllia has good electrical insulating properties and high thermal conductivities; however, its high toxicity restricts its use. Calcium oxide, and to a lesser extent uranium oxide, hydrate readily. The latter, $UO_2$, can be oxidized to lower melting $U_3O_8$. Zirconia in pure form is rarely used in ceramic bodies; however, stabilized or partially stabilized cubic $ZrO_2$ is the most useful simple oxide for operations above 1900°C. Thorium oxide exhibits good properties for high temperature operation but is expensive and radioactive. Titanium oxide is readily reduced to lower oxides and cannot be used in neutral or reducing atmospheres.

### 3.2. Carbon, Carbides, and Nitrides

Carbon (graphite) is a good thermal and electrical conductor. It is not easily wetted by chemical action, which is an important consideration for corrosion resistance. As an important structural material at high temperature, pyrolytic graphite has shown a strength of 280 MPa (40,600 psi). It tends to oxidize at high temperatures, but can be used up to 2760°C for short periods in neutral or reducing conditions. The use of new composite materials made of carbon fibers is expected, especially in the field of aerospace structure. When heated under oxidizing conditions, silicon carbide and silicon nitride [12033-89-5], $Si_3N_4$, form protective layers of $SiO_2$ and can be used up to ca 1700°C (see Nitrides).

Silicon carbide has very high thermal conductivity and can withstand thermal shock cycling without damage. It also is an electrical conductor and is used for electrical heating elements. Other carbides have relatively poor oxidation resistance. Under neutral or reducing conditions, several carbides have potential usefulness as technical ceramics in aerospace application, eg, the carbides (qv) of B, Nb, Hf, Ta, Zr, Ti, V, Mo, and Cr. Ba, Be, Ca, and Sr carbides are hydrolyzed by water vapor.

Silicon nitride has good strength retention at high temperature and is the most oxidation resistant nitride. Boron nitride [10043-11-5] has excellent thermal shock resistance and is in many ways similar to graphite, except that it is not an electrical conductor.

**Table 3. Properties of Pure Refractory Materials**[a]

| | | | | | Mean specific heat | | Thermal conductivity, W/(m·K) | | |
|---|---|---|---|---|---|---|---|---|---|
| Material | CAS Registry Number | Formula | Mp, °C | True specific gravity, g/cm$^3$ | J/(kg·K)[b] | Temp range, °C | 500°C | 1000°C | Linear thermal expansion coefficient per°C × $10^6$, from 20–1000°C |
| aluminum oxide | [1344-28-1] | $Al_2O_3$ | 2015 | 3.97 | 795.5 | 25–1800 | 10.9 | 6.2 | 8.6 |
| beryllium oxide | [1304-56-9] | BeO | 2550 | 3.01 | 1004.8 | 25–1200 | 65.4 | 20.3 | 9.1 |
| calcium oxide | [1305-78-8] | CaO | 2600 | 3.32 | 753.6 | 25–1800 | 8.0 | 7.8 | 13.0 |
| magnesium oxide | [1309-48-4] | MgO | 2800 | 3.58 | 921.1 | 25–2100 | 13.9 | 7.0 | 14.2 |
| silicon dioxide[c] | [7631-86-9] | $SiO_2$ | | 2.20 | 753.6 | 25–2000 | 1.6 | 2.1 | 0.5 |
| thorium oxide | [1314-20-1] | $ThO_2$ | 3300 | 10.01 | 251.2 | 25–1800 | 5.1 | 3.0 | 9.4 |
| titanium oxide | [13463-67-7] | $TiO_2$ | 1840 | 4.24 | 711.8 | 25–1800 | 3.8 | 3.3 | 8.0 |
| uranium oxide | [1344-58-7] | $UO_2$ | 2878 | 10.90 | 251.2 | 25–1500 | 5.1 | 3.4 | |
| zirconium oxide[d] | [1314-23-4] | $ZrO_2$ | 2677 | 5.90 | 460.6 | 25–1100 | 2.1 | 2.3 | 6.5–10 |
| mullite | [55964-99-3] | $3Al_2O_3{\cdot}2SiO_2$ | 1850[e] | 3.16 | 628.0 | 25–1500 | 4.4 | 4.0 | 4.5 |
| spinel | [1302-67-6] | $MgO{\cdot}Al_2O_3$ | 2135 | 3.58 | 795.5 | | 9.1 | 5.8 | 6.8 |
| forsterite | [15118-03-3] | $2MgO{\cdot}SiO_2$ | 1885 | 3.22 | 837.4 | | 3.1 | 2.4 | 9.5 |
| zircon | [10101-52-7] | $ZrO_2{\cdot}SiO_2$ | 2340–2550[f] | 4.60 | 544.3 | | 4.3 | 4.1 | 4.0 |
| carbon | [7440-44-0] | C | | 2.10 | 1046.7 | 25–1300 | 13.4 | 9.9 | 4.0 |
| silicon carbide | [409-21-2] | SiC | 3990[g] | 3.21 | 795.5 | 25–1300 | 22.5 | 23.7 | 5.2 |

[a] Refs. (8–10).

[b] To convert J to cal, divide by 4.184.

[c] Silica glass.

[d] Cubic, stabilized with CaO.

[e] Congruent.

[f] Incongruent.

[g] Dissociates above 2450°C in reducing atmosphere and is readily oxidized above 1650°C.

### 3.3. Borides and Silicides

These materials do not show good resistance to oxidation. Some silicides, however, form $SiO_2$ coatings upon heating which retards further oxidation. Molybdenum disilicide [1317-33-5], $MoSi_2$, is used widely, primarily as an electrical heating element.

### 3.4. Metals

The highest melting refractory metals are tungsten (3400°C), tantalum (2995°C), and molybdenum (2620°C). All show poor resistance to oxidation at high temperatures. Hafnium–tantalum alloys form a tightly adhering oxide layer that gives partial protection up to 2200°C. The layer continues to grow upon extended use.

### 3.5. Phase Equilibria

Phase diagrams represent the chemical equilibria that exist among one, two, or three components of a system under the influence of temperature and pressure (11, 12). Reference to a phase diagram permits the determination of the amount and composition of solid and liquid phases that coexist under certain specified conditions of temperature and pressure for a particular system. Using such information, the occurrence of physical and chemical changes within a system or between systems at high temperatures can be predicted. Systems containing more than three components are difficult or impossible to present graphically; however, mathematical methods have been suggested (13, 14).

Phase diagrams can be used to predict the reactions between refractories and various solid, liquid, and gaseous reactants. These diagrams are derived from phase equilibria of relatively simple pure compounds. Real systems, however, are highly complex and may contain a large number of minor impurities that significantly affect equilibria. Moreover, equilibrium between the reacting phases in real refractory systems may not be reached in actual service conditions. In fact, the successful performance of a refractory may rely on the existence of nonequilibrium conditions, eg, environment (15–19).

### 3.6. Physical Properties

The important physical properties of some refractories are listed in Tables 4, 5, 6, 7. Brick bulk density depends on the specific gravity of the constituents and the porosity. The latter is controlled by the porosity of the raw materials and the brick texture. Coarse, medium, and fine-sized material contribute to the degree of particle packing. Usually the highest density possible is desired. Upon firing, the grains and matrix form glassy, direct, or solid-state ceramic bonds. Sintering is generally accompanied by shrinkage, unless new components are formed that may cause expansion. Differential volume change between the coarse and fine fraction caused by differential sintering rates and formation of addition phases may create stresses. Particle size distribution, forming method, and firing process contribute to texture, whereas permeability is related to porosity, which in turn is dependent upon texture.

### 3.7. Mechanical Properties

The physical properties of a particular refractory product depend on its constituents and manner in which these were assembled. The physical properties may be varied to suit specific applications. For example, for thermal insulations highly porous products are employed, whereas dense products are used for slagging or abrasive conditions.

The transverse strength (modulus of rupture) at room temperature is related to the degree of bonding. Fine-grained refractories generally are stronger than coarse-grained types and those having a low porosity are stronger than those of high porosity. However, the room temperature strength of a refractory is not necessarily indicative of the strength at high temperature because the bond strength may be the result of a glassy phase that softens upon heating.

Generally, high temperature strength is lower than room temperature strength. The former is a measure of the degree of solid-state bonding between refractory grains, whereas high temperature creep indicates the amount of associated liquid or glassy phases and their viscosity. The development of solid-state or direct-bonded basic brick requires high firing temperatures, and is impeded by glassy phases. By referring to phase diagrams, refractory compositions may be designed that avoid the development of such phases.

The modulus of elasticity (MOE) is related to the strength and can be used as a nondestructive quality control test on high cost special refractory shapes such as slide gate valves employed in the pouring of steel (qv). The slide gate type must be selected to ensure chemical compatibility and it must be used in a way to

**Table 4. Composition of Alumina, Silica, and Zirconia Refractories, %[a]**

| Type | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | MgO | Alkalies |
|---|---|---|---|---|---|---|---|
| silica | 95–96 | 0.2–1.5 | 0.8–1.0 | 0.3–0.1 | 3.3–2.7 | $<0.1$ | $<0.2$ |
| fireclay | | | | | | | |
| semisilica | 70–79 | 17–27 | 0.6–2.0 | 0.8–1.6 | 0.1–0.4 | 0.1–0.4 | 0.2–0.4 |
| medium duty | 56–70 | 25–36 | 1.8–3.4 | 1.3–2.7 | 0.2–0.4 | 0.4–0.6 | 1.0–2.7 |
| high duty | 51–59 | 35–41 | 1.5–2.5 | 1.1–3.0 | 0.2–0.6 | 0.1–0.6 | 1.3–2.6 |
| super duty | 50–54 | 40–46 | 0.8–2.3 | 1.1–2.5 | 0.1–0.5 | 0.4–0.6 | 0.1–1.4 |
| high alumina, $Al_2O_3$ | | | | | | | |
| 50% | 40–47 | 47–57 | 0.9–1.6 | 2.2–2.4 | 0.5–0.6 | 0.3–0.6 | 0.8–1.3 |
| 60% | 27–37 | 58–67 | 0.9–2.7 | 1.7–3.0 | 0.1–0.3 | 0.2–0.7 | 0.2–1.2 |
| 70% | 19–28 | 68–77 | 0.9–2.2 | 2.0–3.3 | 0.1–0.3 | 0.1–0.7 | 0.2–1.2 |
| 80% | 8–17 | 78–87 | 0.7–1.7 | 2.5–3.2 | 0.1–0.2 | 0.1–0.4 | 0.1–1.0 |
| 85%[b] | 6–10 | 82–86 | 1.0–2.5 | 2.0–3.0 | trace–0.2 | trace–0.4 | 0.1–0.3 |
| 90% | 3–10 | 88–96 | 0.1–1.4 | 0.1–2.6 | 0.1–0.2 | 0.1–0.3 | trace–0.9 |
| 100% | 0.2–1.1 | 97–99 | 0.1–0.3 | trace–0.3 | 0.1–0.3 | 0.1–0.3 | 0.1–0.3 |
| zircon[c] | 32 | 1 | 0.1 | 1.8 | trace | 0.1 | 0.02 |
| molten cast | | | | | | | |
| $Al_2O_3$–$ZrO_2$–$SiO_2$[d] | 11–13 | 50–51 | trace–1.0 | trace–1.0 | trace | trace | 1.0–1.5 |
| $Al_2O_3$–$SiO_2$ | 18–22 | 57–70 | 1–4 | 3.0–4.5 | 0–1 | 0–1 | 0.0–1.5 |
| $Al_2O_3$ high soda | 0.04 | 93.8 | 0.1 | 0.05 | 0.1 | 0.1 | 5.6 |
| $Al_2O_3$ low soda | 0.10 | 99.2 | 0.1 | 0.05 | 0.1 | 0.1 | 0.3 |

[a] Refs. (2, 5), and (20–23).

[b] Phosphate bonded.

[c] Contains 64% $ZrO_2$.

[d] Contains 33–35% $ZrO_2$.

reduce thermal shock. The performance of a properly selected and used slide gate is directly related to its strength and therefore predicted by its MOE.

### 3.8. Thermal Properties

Refractories, like most other solids, expand upon heating, but much less than most metals. The degree of expansion depends on the chemical composition. A diagram of the thermal expansion of the most common refractories is shown in Figure 1.

### 3.9. Reheat Change

Most refractory bricks are not chemically in equilibrium before use. During the prolonged heating in service, additional reactions occur that may cause the brick to shrink or expand. For instance, 70% $Al_2O_3$ bricks consist of a mixture of corundum grains, mullite, and siliceous glass. In service, the siliceous glass reacts with corundum to form additional mullite, causing expansion. Mullite bricks that contain only mullite are volume stable because equilibrium conditions have been reached during initial firing. Considerable expansion also may be caused by gas formation during heating, for instance, by the decomposition of sulfates. In the presence of a viscous siliceous glass, these gases cannot escape and expansion occurs. This mechanism explains the bloating behavior of common bloating ladle brick. The linear reheat changes of various refractories during an American Society for Testing and Materials (ASTM) reheat test are shown in Tables 5 and 7.

In general, basic brick exhibits good volume stability at high temperatures. Some slight shrinkage may occur in chemically bonded or low fired brick; this shrinkage is most pronounced in high silicate compositions. In high fired, high purity brick containing chrome ore, some expansion on reheat is generated by periclase–spinel

**Table 5. Physical Properties of Alumina, Silica, and Zirconia Refractory Brick**[a]

| | | | Deformation under load[c] | | Linear reheat change[d] | | Thermal spalling loss[e] | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Type | PCE[f] | Modulus of rupture, MPa[b] | Temp, °C | Change, % | at °C | % | at °C | % | Bulk density g/cm$^3$ | Porosity, % |
| silica | | 2.8–11.2 | 1650 | 0 | | | | | 1.60–1.80 | 20–30 |
| fireclay | | | | | | | | | | |
| semisilica | 27–31 | 2.1–4.2 | 1450 | 0.1–2 | | | 1480 | 0–10 | 1.80–2.10 | 20–30 |
| medium duty | 29–31 | 7.0–11.2 | 1450 | 1–6 | | | 1600 | 2–6 | 2.11–2.20 | 17–21 |
| high duty | 31–33 | 2.8–21.0 | 1450 | 0.5–15 | 1600 | 0–1 S | 1600 | 3–7 | 2.13–2.30 | 4–30 |
| super duty | 33–34 | 2.8–24.0 | 1450 | 0–9 | 1600 | 0–1 S | 1650 | 2–8 | 2.28–2.48 | 5–22 |
| high alumina, $Al_2O_3$ | | | | | | | | | | |
| 50% | 34–35 | 7.0–11.2 | 1450 | 2–6 | 1600 | 0–1 E | 1650 | 8–12 | 2.27–2.43 | 14–18 |
| 60% | 36–37 | 7.0–11.2 | 1450 | 1–4 | 1600 | 0–5 E | 1650 | 1–5 | 2.10–2.49 | 13–28 |
| 70% | 37–38 | 7.0–11.2 | 1450 | 1–3 | 1600 | 1–7 E | 1650 | 3–7 | 2.20–2.66 | 14–28 |
| 80% | 38–39 | 7.0–12.6 | | | | | | | 2.50–2.90 | 14–29 |
| 85%[g] | 38–39 | 21.0–35.0 | 1450 | 0.3–3 | 1600 | 0–2 E | 1650 | 0–5 | 2.70–2.92 | 12–17 |
| 90% | 40–41 | 14.0–35.0 | 1700 | 0–1 | 1700 | 0–1 E | 1650 | 0–1 | 2.67–3.10 | 11–27 |
| 100% | 41–42 | 12.6–21.0 | 1650 | 1–2 | 1700 | 0–0.5 S | 1650 | 0–5 | 2.84–3.10 | 19–29 |
| zircon | | | 1600 | 2–5 | 1540 | 0 | | | 3.77 | 20 |
| molten cast | | | | | | | | | | |
| $Al_2O_3$-$ZrO_2$-$SiO_2$ | | | | | | | | | 3.70–3.74 | 0.8–3 |
| $Al_2O_3$-$SiO_2$ | | | | | | | | | 3.00–3.20 | 1–3 |
| $Al_2O_3$ high soda | | | | | | | | | 2.89 | |
| $Al_2O_3$ low soda | | | | | | | | | 3.50 | |

[a] Refs. (2, 5), and (20–23).
[b] To convert MPa to psi, multiply by 145; for kPa, multiply by 0.145.
[c] Load = 172 kPa; % of linear change after 1.5 h.
[d] S = shrinkage; E = expansion.
[e] As determined by ASTM C38.
[f] PCE = pyrometer cone equivalent, as determined by ASTM C24.
[g] Phosphate bonded.

reactions, usually with very complex interdiffusion mechanisms, where the spinel constituents are dissolved in the periclase lattice at high temperature and the spinel phases precipitate from the periclase solid solution on cooling. The expansion may continue with repeated heating and cooling cycles as well as oxidation reduction cycles.

### 3.10. Thermal Conductivity

The refractory thermal conductivity depends on the chemical and mineral composition of the material and increases with decreasing porosity. The thermal conductivities of some common refractories are shown in Figure 2.

### 3.11. Specific Heat

In some applications refractories are used for heat-exchange purposes on the regenerative principle, for instance, in blast-furnace stoves. High heat capacity is required in such applications (Table 8).

**Table 6. Composition of Basic Refractory Bricks, %[a]**

| Type | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Cr_2O_3$ | Residual carbon |
|---|---|---|---|---|---|---|---|
| magnesite | | | | | | | |
| burned | 0.4–4.5 | 0.1–1.0 | 0.1–2.3 | 0.6–3.8 | 91.0–98.0 | 0.0–0.9 | |
| burned, tar impregnated | 0.4–4.5 | 0.1–1.0 | 0.1–2.3 | 0.6–3.8 | 91.0–98.0 | 0.0–0.9 | 2.0–2.5 |
| tar bonded, tempered | 0.5–3.8 | 0.2–1.0 | 0.1–3.0 | 0.9–6.2 | 88.0–98.0 | 0.0–0.4 | 4.2–4.7 |
| resin bonded | 0.5–3.8 | 0.2–1.0 | 0.1–0.5 | 1.5–2.7 | 96.0–97.0 | 0.0–0.2 | 3.8–4.7 |
| high carbon | 0.7–2.3 | 0.1–0.7 | 0.2–0.9 | 0.9–3.0 | 94.0–98.0 | | 7.0–20.0 |
| magnesite–chrome | | | | | | | |
| burned | 1.8–7.0 | 6.0–13.0 | 2.0–12.0 | 0.6–1.5 | 50.0–82.0 | 6.0–15.0 | |
| direct bonded | 1.0–2.6 | 3.0–16.0 | 3.0–10.0 | 0.6–1.1 | 50.0–80.0 | 7.0–20.0 | |
| chemical bonded | 2.0–8.0 | 5.0–14.0 | 2.0–8.0 | 1.0–2.0 | 50.0–80.0 | 6.0–15.0 | |
| chrome | | | | | | | |
| burned | 5.0–8.0 | 27.0–29.0 | 12.0–20.0 | 0.4–1.0 | 15.0–23.0 | 29.0–35.0 | |
| chrome–magnesite | | | | | | | |
| burned | 3.0–5.0 | 8.0–20.0 | 8.0–12.0 | 0.7–1.1 | 40.0–50.0 | 18.0–24.0 | |
| dolomite | | | | | | | |
| burned | 0.8–1.5 | 0.3–0.8 | 0.6–1.5 | 38.0–58.0 | 38.0–58.0 | | 0.0–1.4 |
| tar bonded | 0.3–1.5 | 0.1–0.6 | 0.2–2.0 | 50.0–58.0 | 38.0–43.0 | 0.0–0.3 | 4.0–5.0 |

[a] Refs. (2, 5, 7), and (20–24).

**Table 7. Physical Properties of Basic Brick[a]**

| Type | Bulk density, g/cm$^3$ | Apparent porosity, % | Modulus of rupture, MPa[b] | | Refractoriness under load, shear temp, °C | Linear reheat change[c] at 1650°C, % |
|---|---|---|---|---|---|---|
| | | | 20°C | 1260°C | | |
| magnesite | | | | | | |
| burned | 2.8–3.0 | 15–19 | 7.0–24.5 | 3.5–18.5 | 1590–1760 | 0–4 S |
| burned, tar impregnated[d] | 3.0–3.2 | (13–17)[e] | 20.0–35.0 | 10.5–21.0 | | |
| tar bonded, tempered | 3.0–3.1 | 3–7 | 7.0–11.0 | | 1700+ | |
| resin bonded | 2.9–3.1 | 4–7 | 8.0–27.0 | | | |
| high carbon | 2.7–3.0 | 1–6 | 7.0–9.0 | | | |
| magnesite–chrome | | | | | | |
| burned | 2.9–3.0 | 17–20 | 3.0–4.9 | 0.7–2.0 | 1500–1700 | 0–0.3 S |
| direct bonded[f] | 2.9–3.2 | 14–19 | 5.6–13.9 | 8.4–17.5 | 1700+ | 0.7 S–1.0 E |
| chemical bonded | 3.0–3.2 | 18–20 | 7.0–14.0 | 0.7–2.8 | 1650–1760 | 1 S–5.0 S |
| chrome | | | | | | |
| burned | 3.1–3.3 | 18–20 | 6.0–14.0 | 0.4–1.1 | 1260–1370 | 0–0.6 S |
| chrome–magnesite | | | | | | |
| burned | 3.0–3.2 | 19–21 | 5.6–8.4 | 2.8–11.2 | 1650–1700 | 0–0.1 E |
| dolomite | | | | | | |
| burned | 2.7–3.1 | 6–19 | 7.0–32.8 | | 1700+ | 0–0.2 S |
| tar bonded | 2.8–3.0 | (8–12)[e] | 7.0–11.0 | | | |

[a] Refs. (2, 5, 7, 20–23), and 25.

[b] To convert MPa to psi, multiply by 145.

[c] S = shrinkage; E = expansion.

[d] 7.0–16.0 MPa at 1480°C.

[e] Obtained on ignited sample.

[f] 2.0–4.2 MPa at 1480°C.

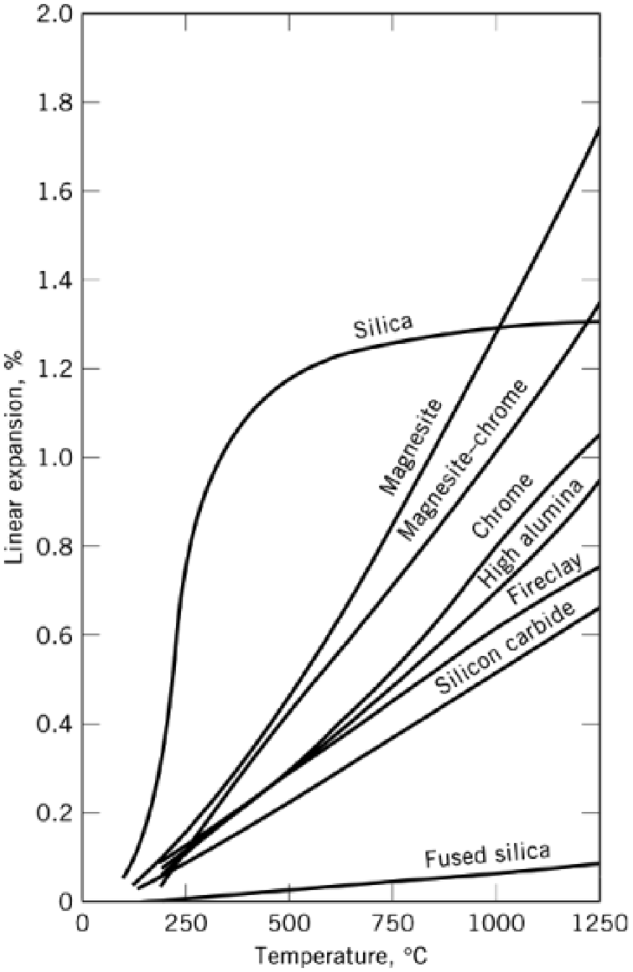

**Fig. 1.** Thermal expansion values of some materials.(Courtesy of *Chemical Engineering* (28).)

### 3.12. Thermal Spalling

Refractories are brittle and stresses caused by sudden variations in temperatures can cause cracking and destruction. The susceptibility to thermal cracking and spalling depends on certain characteristics of the raw material and the macrostructure of the particular refractory. Spalling resistance may be increased by either preventing cracks from forming or preventing cracks from growing. The approach used to effect spall resistance determines which properties of the refractory are optimized. Generally low thermal expansion, high density and high thermal conductivity, and high strength refractories exhibit good thermal shock resistance. Fireclay and high alumina refractories usually have a higher resistance to thermal shock than periclase refractories. Dense strong bodies withstand high stress and transmit it over large volumes; when failure occurs it is serious. Weak porous bodies, however, tend to crack before catastrophically large stresses are generated and thus are much less seriously damaged and generally remain intact.

The resistance against thermal spalling of fireclay and high alumina brick is indicated in Table 5. No standard test has been adopted for basic brick. Refractories composed of 100% magnesia exhibit poor thermal

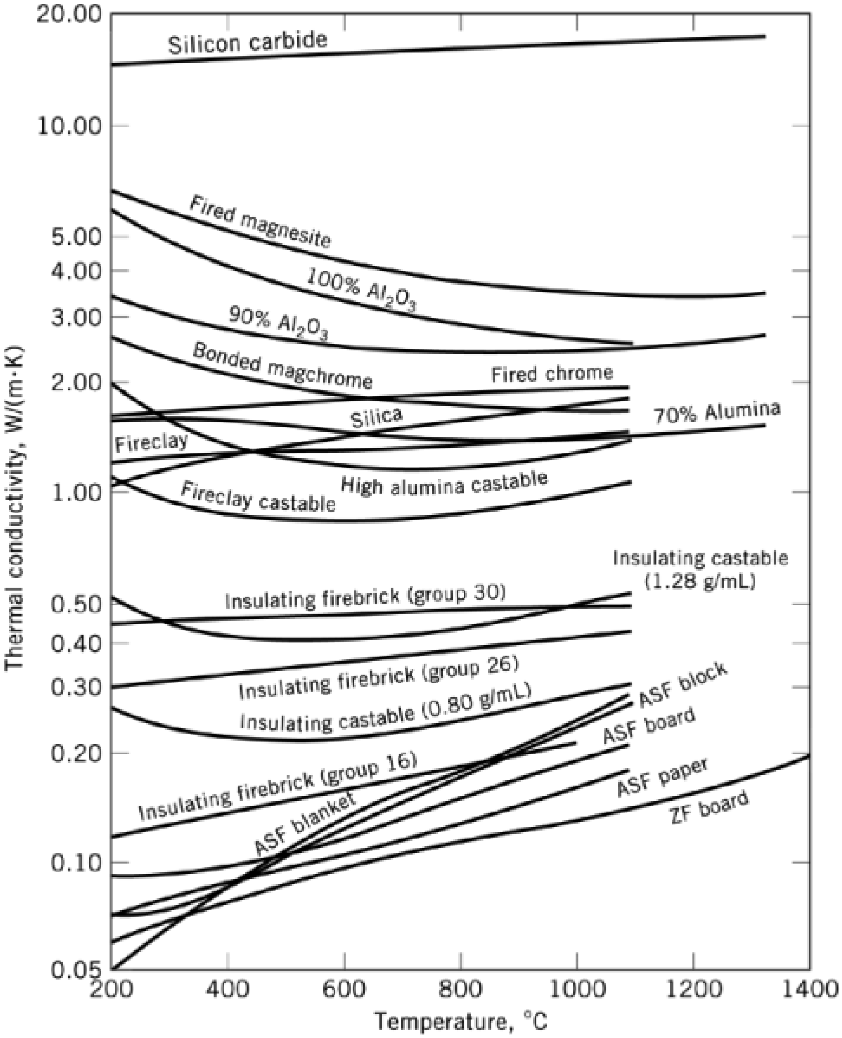

**Fig. 2.** Thermal conductivity of refractories where $_{ASF=}$ aluminosilicate fiber and $_{ZF=}$ zirconia fiber. See Table 13 for group classifications (5, 25).

shock resistance, which is improved by addition of chrome ore. So-called direct bonded basic brick, composed of magnesia and chrome additions, exhibits good thermal shock resistance.

### 3.13. Refractoriness

Most refractories are mixtures of different oxides, sometimes with significant quantities of impurities. Thus, they do not have sharp melting points but a softening range. Refractoriness is the resistance to physical deformation under the influence of temperature. It is determined by the pyrometric cone equivalent (PCE) test for aluminosilicates and resistance to creep or shear at high temperature (see Analytical methods).

**Table 8. Mean Specific Heats of Refractory Brick and Minerals, Between 0°C and the Indicated Temperature, J/(kg·K)**[a,b]

| | Brick | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Temp, °C | Fireclay | Silica | Magnesite | Chrome | Forsterite | Mullite | Cristobalite | Periclase | Corundum |
| 0 | 249.5 | 218.5 | 268.9 | 219.8 | 232.9 | 237.9 | 213.3 | 268.9 | 221.1 |
| 93 | 257.3 | 243.0 | 283.1 | 227.5 | 258.5 | 248.2 | 236.6 | 293.5 | 253.4 |
| 204 | 266.4 | 272.8 | 300.0 | 235.3 | 279.3 | 276.7 | 263.8 | 310.3 | 276.7 |
| 316 | 274.1 | 296.1 | 312.9 | 243.1 | 297.4 | 288.3 | 309.0 | 324.5 | 292.2 |
| 427 | 284.5 | 307.7 | 324.5 | 250.8 | 310.3 | 296.1 | 324.5 | 332.3 | 303.9 |
| 538 | 293.5 | 318.1 | 333.6 | 257.3 | 318.1 | 301.3 | 333.6 | 338.8 | 312.9 |
| 649 | 302.6 | 325.8 | 340.1 | 259.9 | 323.3 | 306.4 | 341.4 | 345.2 | 320.7 |
| 760 | 311.6 | 333.6 | 346.5 | 268.9 | 328.4 | 310.3 | 346.5 | 349.1 | 325.8 |
| 871 | 320.7 | 336.2 | 353.0 | 274.1 | 333.6 | 312.9 | 350.4 | 354.3 | 332.3 |
| 982 | 327.1 | 341.4 | 359.5 | 279.3 | 338.8 | 316.8 | 353.0 | 358.2 | 336.2 |
| 1093 | 333.6 | 346.5 | 365.9 | 284.5 | 343.9 | 319.4 | 355.6 | 362.0 | 341.5 |
| 1204 | 338.8 | 351.7 | 372.4 | 287.0 | 349.1 | 322.0 | 358.2 | 364.6 | 345.2 |
| 1316 | 343.9 | 356.9 | 378.8 | 289.6 | 354.3 | 324.5 | 359.5 | 368.5 | 349.1 |
| 1427 | 347.8 | 360.7 | 384.0 | 292.2 | 359.5 | 327.1 | 360.7 | 372.4 | 353.0 |
| 1538 | | | | | | 329.7 | 362.0 | 375.0 | 356.9 |
| 1642 | | | | | | 331.0 | 363.3 | 377.6 | 360.7 |
| 1760 | | | | | | 333.6 | | 380.1 | 364.6 |

[a] Ref. 26.
[b] To convert J/(kg·K) to Btu/(lb·°F), multiply by $2.39 \times 10^{-4}$.

## 4. Manufacture

### 4.1. Processing

Initial processing may include an extensive survey of the deposit, selective mining, stockpiling by grade, and beneficiation techniques such as weathering, grinding, washing, heavy-media separation, froth flotation, etc. Some materials can be used without further processing although many must be subjected to heat treatment. In the case of synthetic grain, the selected and beneficiated raw materials are blended in the desired proportions and formed into suitable shapes for calcination by briquetting, pelletizing, or extrusion. Slurries may be calcined; however, this practice is avoided in the interest of fuel economy. Originally, calcination referred specifically to the treatment of calcareous minerals to remove $CO_2$. The term has come to be used to indicate heat treatment to sinter or burn (dead burn) the refractory grain to a stable dense material as well as to decompose minerals. Calcination may be carried out to rotary kilns, shaft kilns, multiple-hearth furnaces, or fluidized-bed reactors. The last two devices are reserved for relatively light calcining. The particular feed is dictated by the kiln type and the precalcination processes to which the raw materials or mixes may have been subjected. These hard, burned materials are called grain, clinker, or grog, a term also used for ground firebrick. Low density or expanded aggregates can be made by burning clay or clay mixtures that evolve gas during burning and thereby expand or produce porosity. The burn-out material may be naturally present in the clay or mixed with the clay before burning.

Both raw and processed materials can be fused or melted in electric-arc furnaces. These materials can be melted and then cast into shapes, formed in the furnace itself as an ingot, or formed into fibers. Partially fused ingots are crushed into grains. Because these ingots are not homogeneous, the grains have to be graded; the middle portion is purer than the outside material which is less well fused. Melts used for casting or fiber forming are homogeneous.

### 4.2. Crushing and Grinding

Some raw materials, such as hard clay and quartzite, must first be crushed to grains small enough for the grinding equipment. In general, a jaw, gyrotory, or roll crusher is employed (see Size reduction).

Almost all raw materials require grinding after primary crushing. For coarse grinding, a dry pan or occasionally a wet pan is used. The dry pan is similar to a grist mill but has a perforated bottom through which the crushed material is continuously removed. The wet pan is similar, but has a solid bottom. For very fine grinding, a ring-roll, ball, or impact mill is employed.

### 4.3. Screening

To obtain a high density product, the mix is made from materials that have been sized into classes by means of standard screens. In a continuous screening operation, the ground raw materials are generally fed to vibrating high capacity screens that may be heated. Material that does not pass the screen is returned to the grinding system for further size reduction. Coarse and medium fine-grain sizing is accomplished by the aforementioned methods, whereas fine-sized materials generated in rod mills, ball mills, ring-roll mills, etc, are classified by air separators. A single screen with uniform openings produces a single product referred to as a straight grind. For closer control of a mix, screen analysis-sized fractions are used to produce the overall desired particle size distribution. Here a series of two, three, or more vibrating screens are set in stacks yielding a coarse band, an intermediate band, and a fine band. These fractions are blended into the mix in the proper proportions to provide the desired particle packing. The distribution may be continuous following either distributions proposed by Furnas, Andreason, or the modified Andreason distribution or may be discontinuous or semicontinuous gap-grain sizing. The use of a particular distribution depends on a variety of factors such as the degree of plasticity of the mix constituents, the method of forming to be used, and the requirement for density and thermal shock resistance. A typical brick formulation may contain 50% coarse (ranging from 0.625 cm to fine sand) and about 20% less than 44 $\mu$m (similar to fine flour) material.

### 4.4. Mixing

As in other ceramic processes, more than one type of raw material is often required for a refractory product. The purpose of mixing is to uniformly distribute the various ingredients (see Mixing and blending). Although the specific steps and equipment involved in the mixing of batches for fireclay, high alumina, and basic refractories are somewhat different, the general principles are similar. Mixes that are to be dry-pressed contain 2–6% binding liquid, depending on the plasticity of the raw material bond system and the fineness of the mix. The ingredients may be blended in a pug mill, dry pan, or other type mixer and tempered with the bonding ingredients. Tempering, in the sense used here, denotes the kneading action produced on the mix, usually in a muller mixer. Mixes to be extruded or hand formed contain 10–20% liquid. These mixes may be prepared in a pug mill or wet pan.

The mixing of tar-, resin-, and chemically bonded brick material presents special problems. Tar- and resin-bonded mixes are usually basic compositions. Because coal-tar and petroleum pitches have ring-and-ball values of ca 100°C, ie, the softening point as determined by ASTM D30, provisions for mixing the ingredients at elevated temperatures must be made. Typically, the grain is heated to ca 150°C and maintained at that temperature while the hot pitch is added. After a preset mixing time, the batch is transferred to the pressing equipment. For resin-bonded mixes, the grain does not have to be heated, although liquid resins may be heated to enhance their flow characteristics. Phenolic (phenol–formaldehyde), alkyd–oil–urethane, urea–formaldehyde, furan resins, etc, are used (see Alkyd resins; Amino resins and plastics; Phenolic resins). Resin-bonding systems are more expensive than pitches, but concerns regarding potential health risks of pitch fumes have renewed interest in resins.

Chemically bonded basic bricks are blended much the same as burned brick mixes except that a bonding agent, eg, magnesium sulfate or magnesium chloride, is added to the mix as well as tempering water to form oxysulfates or oxychlorides.

### 4.5. Forming

Most refractory shapes are formed by mechanical equipment, but some very large or intricate shapes require hand molding in wooden, steel-lined molds with loose liners to permit easy removal of plaster of Paris molds.

A few fireclay refractories are produced by the stiff-mud process using an auger machine that pugs, de-airs, and continuously extrudes a clay column. A wire cutter cuts the clay into blanks which are then sized, shaped, and branded by a repress machine.

Refractory shapes are generally produced on a mechanical toggle press, screw press, or hydraulic press. In this operation, a mold cavity is filled with the damp mix. During the pressing cycle, some products such as fireclay brick are de-aired by applying a vacuum to the top and bottom press heads which contain a series of small openings. De-airing promotes a denser product and reduces lamination. In some basic presses, bricks are encased in steel or have internal steel plates which are placed in the mold box before charging; the plates become an integral part of the brick upon pressing. Plates may also be bonded to the brick after pressing. From one to four bricks may be pressed at a time, depending on the size. Pressures range from ca 17 (2500) to ca 98 MPa (14,000 psi) for plastic firebrick or nonplastic basic mixes, respectively. Pitch-bonded brick must be formed hot. Initial heating of the press may be required, but the residual heat from the mix is usually sufficient to maintain the necessary temperature. Another type is the impact- or jolt-mold press that consists of a mold box and press heads activated by pneumatic cylinders, eg, jack hammers. Some special shapes are produced by air-ramming which is similar to hand molding, except that reinforced steel molds are required and the damp mix is slowly fed to the mold while molders manually compact the material with pneumatic rammers. Special shapes can also be formed by slip casting and hot pressing.

Fusion-cast refractories are formed by first melting the material in an electric arc. The liquid is poured into a mold and allowed to cool. Various annealing processes and refining techniques ensure a uniform and structurally sound shape. The case form is then cut or ground to size.

Fused-cast refractory is very dense but may contain a system of closed pores and large, highly oriented grains may exist in a particular casting. The size and distribution of the pore and grain phases must be controlled.

Isostatic pressing gives a highly uniform product, although the production rate is somewhat low. It typically contains very small grains and little or no porosity. In this process, a rubber sock or bag of the desired shape is filled with the refractory mix. The sock is then subjected to extremely high pressure in a hydraulic pressure chamber.

Large and small shapes may be slip cast from both plastic and nonplastic mixes by the usual techniques. Precise shapes, such as glass feeder parts, are made in this way as well as large flux blocks. The process requires the formulation of a slip of suitably stable character to be poured into a plaster mold to be dewatered. After it solidifies, the mold is removed and dried further before firing.

### 4.6. Drying

The drying (qv) step for large shapes is critical. Extremely large fireclay and silica shapes are sometimes allowed to dry on a temperature-controlled floor heated by steam or air ducts embedded in the concrete. Smaller shapes are generally dried in a tunnel dryer. The ware is placed on cars that enter the cold end and exit at the hot end. These dryers may be humidity-controlled and are heated by their own source or with waste heat from the burning operation. Microwave and infrared drying are being investigated.

Pitch-bonded and resin-bonded bricks are treated or cured in special ovens at temperatures higher than that used for drying other types of bricks. Pitch-bonded brick is cured at 230–320°C; this process is called tempering which is not to be confused with tempering during mixing. Tempering removes some of the volatiles from the pitch and eliminates or reduces thermoplastic or slumping behavior in service (see Drying).

### 4.7. Curing

Some chemically bonded bricks require some elevated heat treatment that is typically higher than the tempering process mentioned above, but less temperature than that required to form ceramic bonds. One example is aluminosilicate brick bonded with phosphoric acid. A very strong bond can be developed with heat treatment temperatures above 600°C. Even though adequate strengths can be obtained at low temperatures, complete curing of even these refractories may be desired for certain applications.

#### *4.7.1. Burning*

Bricks are fired or burned in kilns to develop a ceramic bond within the refractory and attain certain desired properties. This step does not apply to chemically or organically bonded products. Preferred for this purpose is the continuous or tunnel kiln, a structure of narrow cross section and 61–183 m in length. The bricks are set on cars that move slowly through the kiln, which is divided into the preheating, burning, and cooling zones. The length of the zones controls the rates of heating and cooling, and the time at temperature (soak time). The temperature in the firing zone ranges from 1000 to 1700°C. Gas, oil, or coal may be used as a fuel. Where the quantities of refractories being fired is too small for use of a tunnel kiln, periodic or shuttle kilns are used.

Silica brick and large fireclay shapes are fired in circular downdraft kilns. These kilns vary in diameter and can accommodate up to 150,000 23-cm bricks or their equivalent in other sizes. The complete burning cycle for a typical periodic kiln ranges from 21 to 27 days as compared with four to seven days for a tunnel kiln.

The shuttle kiln consists of a firing chamber with two or more kiln cars on which the bricks to be fired are set. While one load of brick is being fired, a second is being set. Somewhat similar is the bell top or top-hat kiln which is raised and lowered above and over the kiln cars to be fired. These kilns are more expensive to operate than tunnel kilns but provide flexibility in burning conditions and production schedules.

Burned brick may be impregnated with tar or pitch to improve corrosion resistance. The heated bricks are placed in the impregnation unit which is sealed and evacuated to remove air from the pores of the refractory. The evacuated chamber is then filled with hot pitch and the vacuum is released. The treated product is allowed to drain free of excess pitch and is ready for shipment. Although this treatment is primarily used on basic refractories, it can be extended to other classes. The benefits derived from impregnation are lost if the pitch is burned off at high temperature; therefore, a reducing atmosphere is required such as is encountered in a basic oxygen steelmaking furnace.

### 4.8. Specialty Refractories

Bulk refractory products include gunning, ramming, or plastic mixes, granular materials, and hydraulic setting castables and mortars. These products are generally made from the same raw materials as their brick counterparts.

Granular materials are shipped raw or calcined and usually have been ground to a specified screen size or size distribution. The additives depend on the application and service conditions. These materials are used in construction, repair, or maintenance of furnaces and vessels. Refractory mortars are used to lay brick of the same composition. These are manufactured wet premixed or dry.

Ramming mixes and plastics are manufactured similarly to brick; that is, the coarse refractory aggregate is added to a wet pan and combined with a small amount of raw clay or organic agents for plasticity. Water is added to the batch; refractory plastics generally contain more water and raw clay than ramming mixes. After

**Table 9. Distribution of U.S. Refractory Sales**[a]

| | U.S. sales, % of total | | | | |
|---|---|---|---|---|---|
| Industry | 1964 | 1977 | 1979 | 1985 | 1986[b] |
| iron and steel | 61.2 | 47.2 | 51.6 | 49.4 | 49.0 |
| nonferrous metals | 5.4 | 6.1 | 7.5 | 8.2 | 7.5 |
| cement | 2.0 | 3.6 | 4.9 | 4.3 | 4.1 |
| glass | 5.3 | 4.6 | 5.1 | 4.7 | 6.4 |
| ceramics | 5.0 | 8.7 | 9.7 | 8.1 | 8.3 |
| chemical and petroleum | 3.0 | 2.5 | 2.1 | 3.3 | 3.5 |
| public utilities | 1.1 | 0.7 | 0.9 | 1.2 | 0.8 |
| export | 5.3 | 6.5 | 7.4 | 4.9 | 5.1 |
| all other | 11.7 | 20.1 | 10.9 | 16.4 | 15.2 |
| Total, $\$ \times 10^6$ | 497.0 | 1299.0 | 1727.0 | 1580.0 | 1520.0 |

[a] Ref. 31.

[b] Last year production data reported by industry; see ASTM C28.

discharge from the wet pan, plastic mixes are formed by extrusion into 25-kg blocks and sliced into rectangular slabs. The material was historically packaged damp and ready for installation with pneumatic rammers. Dry plastic mixes requiring on-site mixing are available. Ramming mixes are generally shredded into small lumps and placed damp in airtight steel drums ready for installation with pneumatic rammers. Ramming mixes are also available in dry form for mixing on-site. When installed, ramming mixes generally require forms to contain the material as it is rammed. Plastics, however, are soft and cohesive and can be installed without forms, although supporting anchors for vertical and in some cases horizontal installations are used.

Basic raw materials are susceptible to hydration and therefore specialty products are shipped dry and mixed with water on-site for gunning or ramming. Certain basic specialties are offered with organic vehicles such as oils and can be used without on-site mixing. Information on manufacturing can be found in References (26–30).

## 5. Economic Aspects

The principal consumers of refractories are the iron (qv) and steel (qv) industries (Table 9). The decrease in refractories consumption coincides with technological changes in the manufacture of steel. First, in the 1960s, open-hearth steelmaking was replaced by the basic oxygen furnace (BOF). Steady improvements in BOF practice and improvements in refractory composition and design has led to improved refractory performance. Early BOF furnaces would be campaigned for 100 heats before relining. As of the mid-1990s, 3000 heats and more are typical. More sophisticated ladle metallurgical practice has been employed leading to improved steel quality and improved refractory performance. The values of shipped refractories from 1970 through 1993 are given in Table 10.

The number and dollar sales values of brick equivalents of shaped refractories are given in Table 11. There was a large drop in refractory shipments at the beginning of the 1980s that corresponded to a reduction in steel plant capacity by almost half during that period. Large steelmaking complexes were called integrated shops because they were designed to integrate the ironmaking and steelmaking of a steel product stock in one large complex. Since the 1980s these shops have given way to more specialized, much smaller steel shops called minimills. Steel production has increased from the 1980 level but the main change has been the quality improvement of steel resulting from the change to ladle metallurgical processes such as ladle refining, vacuum processing, and the growth of the so-called minimills, based on electric furnace shops instead of the large integrated steel plants (see Steel).

**Table 10. Refractories Shipped, 1970–1993 $10^6$[a]**

| Year | Refractory |  | Total |
|---|---|---|---|
|  | Clay | Nonclay |  |
| 1970 | 256 | 342 | 599 |
| 1973 | 327 | 453 | 780 |
| 1976 | 464 | 621 | 1084 |
| 1979 | 712 | 1015 | 1727 |
| 1980 | 512 | 698 | 1211 |
| 1985 | 695 | 888 | 1582 |
| 1990 | 772 | 1232 | 2202 |
| 1993 | 749 | 1163 | 1912 |

[a] Ref. 31.

**Table 11. Shipments of Shaped Refractories[a, b]**

| Year | Fireclay[c] |  | High alumina[d] |  | Silica |  | Basic[e] |  |
|---|---|---|---|---|---|---|---|---|
|  | $10^6$ E | $10^6$ \$ | $10^6$ E | $10^6$ \$ | $10^6$ E | $10^6$ \$ | $10^6$ E | $10^6$ \$ |
| 1965 | 614 | 102 | 56 | 41 | 110 | 21 | 140 | 124 |
| 1975 | 507 | 142 | 129 | 137 | 41 | 32 | 126 | 279 |
| 1985 | 172 | 167 | 98 | 234 | 6 | 15 | 54 | 247 |
| 1993 | 144 | 164 | 118 | 231 | 21 | 32 | 76 | 418 |

[a] Ref. 31.

[b] E = brick equivalents.

[c] Includes regular fireclay, semisilica superduty fireclay, ladle brick, and insulating firebrick (IFB) below 23.

[d] Includes high alumina, mullite, and extra high alumina brick.

[e] Includes magnesite, magnesite–chrome, chrome, chrome–magnesite brick, and dolomitic brick.

## 6. ASTM Classifications and Specifications

### 6.1. Classifications

In addition to testing methods, ASTM publishes a list of classifications covering a wide variety of refractory types (32). The various brands from numerous producers and producing districts are grouped into classes using a nomenclature indicative of chemical composition, heat resistance, and service properties. The number of refractories being developed has been large. The classifications may be inadequate to encompass all refractories encountered, but these represent the only universally accepted standards specifying composition or properties. A more general classification of refractory form and type is also available (33).

#### *6.1.1. Fireclay and High Alumina Brick*

ASTM designation C27 covers fireclay and high alumina brick (Table 12). High alumina brick is classified according to alumina content, starting at 50% and continuing up to 99% $Al_2O_3$. Manufacturers are allowed 2.5% of the nominal alumina content, except for 85 and 90% (2.0%) and 99% (min 97%). An additional requirement for alumina bricks with $Al_2O_3$ content of 50, 60, 70, and 80%, are pyrometer cone equivalents (PCEs) of 34, 35, 36, and 37, respectively.

#### *6.1.2. Basic Brick*

Chrome brick, chrome–magnesite brick, magnesite–chrome brick, and magnesite brick are classified under ASTM C455. There are six classes of chrome–magnesite and magnesite–chrome brick starting with 30% MgO and increasing in 10% increments to 80% MgO. The minimum requirement for MgO is 5% less than the nominal

**Table 12. ASTM C27 Fireclay Brick Classification[a]**

| Classification | Type | PCE[b] | Panel spalling loss, max, % | Cold modulus of rupture, MPa[c] | Other test requirements |
|---|---|---|---|---|---|
| superduty | regular[d] | 33 | 8 at 1650°C | 4.14 | |
| | spall-resistant[d] | 33 | 4 at 1650°C | 4.14 | |
| | slag-resistant | 33 | | 6.89 | bulk density, min, 2.243 g/cm$^3$ |
| high duty | regular | $31\frac{1}{2}$ | | | |
| | spall-resistant | $31\frac{1}{2}$ | 10 at 1600°C | 3.45 | |
| | slag-resistant | $31\frac{1}{2}$ | | 8.27 | bulk density, min, 2.195 g/cm$^3$, or max porosity 15% |
| semisilica[e] | | | | 2.07 | silica content, min, 72% |
| medium duty | | 29 | | 3.45 | |
| low duty | | 15 | | 4.14 | |

[a] Ref. 34.

[b] PCE = pyrometer cone equivalent.

[c] To convert MPa to psi, multiply by 145.

[d] Reheat shrinkage at 1600°C is 1.0% max.

[e] Hot-load subsidence at 1350°C is 1.5% max.

**Table 13. ASTM C155 Insulating Brick Classification[a]**

| Group identification number | Test temperature for $\leq 2\%$ reheat change, °C (°F) | Bulk density, $<$ g/cm$^3$ |
|---|---|---|
| 16 | 815 (1550) | 0.545 |
| 20 | 1065 (1950) | 0.641 |
| 23 | 1230 (2250) | 0.768 |
| 26 | 1400 (2550) | 0.865 |
| 28 | 1510 (2750) | 0.961 |
| 30 | 1620 (2950) | 1.089 |
| 32 | 1730 (3150) | 1.522 |
| 33 | 1790 (3250) | 1.522 |

[a] Ref. 34.

percentage MgO specified for each class. For the three magnesite classes for 90, 95, and 98% MgO the minimum requirement is 86, 91, and 96% MgO, respectively. A chrome brick is manufactured entirely of chrome ore.

### 6.1.3. Insulating Brick

ASTM classifies insulating firebrick under C155 by group. The group number corresponds to the service temperature divided by 100 (Table 13). For example, group 16 corresponds to a test temperature of ca 1600°F (871°C).

### 6.1.4. Mullite Refractories

Mullite refractories are classified under ASTM C467. This brick must have an $Al_2O_3$ content between 56 and 79% and contain less than 5% impurities. Impurities are considered metal oxides other than those of aluminum and silicon. The hot-load subsidence is 5% max is 1593°C.

### 6.1.5. Silica Brick

Under ASTM C416, types A and B silica bricks are classified according to chemical composition and strength. Silica brick must have an average modulus of rupture of 3.5 MPa (500 psi), $<1.5\%$ $Al_2O_3$, no more than 0.2%

$TiO_2$, $<2.50\%$ $Fe_2O_3$, and $<4.00\%$ CaO. Type A brick must have a flux factor $\leq 0.5$. The flux factor is equal to the percent alumina plus twice the percent of alkalies. Type B are all other silica brick covered by the standard chemical and strength specifications.

### *6.1.6. Zircon Refractories*

ASTM C545 classifies zircon refractories in two types. Types A and B have the same chemical requirements of not less than 60% $ZrO_2$ and not less than 30% $SiO_2$. Type A (regular) must have a density of less than 3.85 g/cm$^2$ and type B (dense) more than 3.85 g/cm$^2$.

### *6.1.7. Castable Refractories*

Hydraulic-setting refractory castables are classified under ASTM C401 into five classifications: Regular Castable Refractory, Low Cement Castable Refractories, Ultra-Low Cement Castable Refractories, No-Cement Castable Refractories, and Insulating Castable Refractories. The regular castable class contains hydraulic setting cement and has a total calcium oxide content greater than 2.5%. This class is subdivided into a normal strength and high strength class which have strengths, as measured by modulus of rupture, of 2.07 and 4.14 MPa (300 and 600 psi), respectively. Each is further classified into subgroups A through G on the basis of shrinkage as shown (34).

| Class | 5-h Firing temp after which $\leq 5\%$ shrinkage permitted, °C |
|---|---|
| A | 1095 |
| B | 1260 |
| C | 1370 |
| D | 1480 |
| E | 1595 |
| F | 1705 |
| G | 1760 |

Low Cement, Ultra-Low Cement, and No-Cement Castables are classified on the basis of calcium oxide content. These are 1–2.5, 0.2–1.0, and 0.2% CaO maximum, respectively. In the latter case the lime content is not a result of a hydraulic setting cement constituent but comes from aggregate impurities. The insulating class is also subdivided. This division is shown in Table 14. Refractories used in steel-pouring pits are classified under ASTM C435 (Table 15).

**Table 14. Classification of Insulating Castables**[a]

| Class | 5-h Firing temp after which $\leq 5\%$ shrinkage permitted, °C | Density, g/cm$^3$ |
|---|---|---|
| N | 925 | 0.88 |
| O | 1040 | 1.04 |
| P | 1150 | 1.20 |
| Q | 1260 | 1.44 |
| R | 1370 | 1.52 |
| S | 1480 | 1.52 |
| T | 1595 | 1.60 |
| U | 1650 | 1.68 |
| V | 1760 | 1.68 |

[a] Ref. 34.

**Table 15. ASTM C435 Classification For Steel-Pouring Pit Refractories**[a]

| Class | Type | PCE[b] | Porosity[c], % | Reheat change[c] above 1350°C, %[d] |
|---|---|---|---|---|
| nozzle | A | 15–20 | 8 | 1.0 |
| | B | 20–29 | 8 | 1.0 |
| | C | 29[c] | 10 | 1.0[e] |
| sleeve | A | 15–20 | 10 | 1.0 |
| | B | 20–29 | 10 | 1.0 |
| | C | 29[c] | 10 | 1.0[e] |
| laddle brick[f] | A | 15[c] | 18[e] | 5.0[g] |
| | B | 15[c] | 18[e] | 2.5 |
| | C | 26[c] | 18[e] | 0.5[e,h] |

[a] Ref. 34.
[b] PCE = pyrometer cone equivalent.
[c] Value is minimum unless otherwise indicated.
[d] Except ladle brick which is heated as stated; min refers to expansion, and max to shrinkage of diameter.
[e] Value is maximum.
[f] Modulus of rupture of 4.83 MPa (700 psi) required.
[g] Above 1290°C.
[h] Above 1500°C.

### 6.2. Specifications

Among the many specifications covering refractory products, the best known are those published by ASTM. In addition, specifications are issued by the U.S. Government and the armed forces. The former are generally preceded by the prefix HH and the later by the prefix MIL. The ASTM refractory specifications always suggest a use, whereas federal and military specifications are inconsistent in this respect.

No less important are specifications issued by industrial consumers. Consumers are making purchasing decisions on the basis of the manufacturer's processing capability and requiring the inspection of production control charts and data.

The International Organization for Standardization (ISO) has issued the ISO 9000 series standards for quality management and quality assurance requirements and guidance. These standards are being rapidly adopted as national standards. Companies wishing to compete within regional trading groups are being required to apply these standards to their manufacturing operations (see Materials standards and specifications; Quality assurance).

## 7. Analytical and Test Methods

The test methods applicable to refractories are available (34). These methods are summarized in Table 16.

### 7.1. Refractoriness

Refractoriness is determined by several methods. The pyrometric cone equivalent (PCE) test (ASTM C24) measures the softening temperature of refractory materials. Inclined trigonal pyramids (cones) are formed from finely ground materials, set on a base, and heated at a specific rate. The time and temperature (heat treatment) required to cause the cone to bend over and touch the base is compared to that for standard cones.

The standard ASTM PCE test is relative and used extensively only for alumina–silica refractories and raw materials (see Table 5). However, the upper service limit is generally several hundred degrees below the

**Table 16. ASTM Test Methods for Refractories[a]**

| Material | Test identification | Properties |
|---|---|---|
| burned brick | C20, C830 | apparent porosity, water adsorption, bulk density |
| brick, various shapes | C133, C607, C93 | crushing strength, modulus of rupture |
| basic brick | C456 | hydration resistance |
| brick and tile | C154 | warpage |
| granules | C357, C493 | bulk density |
| periclase grains | C544 | hydration |
| mortar | C198 | cold-bonding strength |
| air-setting plastics | C491 | modulus of rupture |
| castables | C298 | modulus of rupture |
| granular dead-burned dolomite | C492 | hydration |
| fireclay plastics | C181 | workability index |
| castables | C417 | thermal conductivity |
| plastics | C438 | thermal conductivity |
| general refractories | C288 | disintegration in CO atmosphere |
|  | C135 | true specific gravity |
|  | C201 | thermal conductivity |
|  | C92 | sieve analysis and water content |

[a] Ref. 34.

nominal PCE temperature because some load is generally applied to the refractory during service. In addition, chemical reactions may occur that alter the composition of the hot face and therefore the softening point. The relationship between PCE numbers and temperature is described in ASTM C24.

Another measure of refractoriness is the hot-compressive strength or hot-load test for refractory bricks or formed specialties. The specimen carries a static load from 69 kPa (10 psi) to 172 kPa (25 psi). It is heated at a specific rate to a specific temperature which is then held for 1.5 h, or it is heated at a specific rate until it fails. The percent deformation or the temperature of failure is measured. The procedure is described in ASTM C16.

### 7.2. Thermal Strength and Stability

Dimensional changes that occur upon reheating can be determined by ASTM C605, C210, C179, or C113. Specimens are selected and cut or formed to an appropriate size and measured before and after being heated at an appropriate temperature schedule to a specified temperature for 5 to 24 hours. The linear, diametral, or volume percentage change is noted.

High temperature strength of refractory materials is determined on rectangular prisms $25 \times 25 \times 150$ mm cut from the product being tested. The specimens are placed in a furnace, heated to a desired temperature, and the modulus of rupture is determined. A detailed description is given in ASTM C583.

Thermal spalling resistance is determined by ASTM C439, C122, C107, and C38. The last three methods apply to fireclay, high alumina bricks, and plastics using the apparatus described in C38. The specimens are weighted and built into a panel (wall section) that was preheated for 24 h at a specific temperature. The panels are then subjected to 12 cycles of heating to 1400°C followed by cooling with water and air spray. The panel is dismantled, the loose spalls are removed, and the weight loss is recorded as percent spalling loss. Thermal spalling of silica brick is determined on six specimens placed on a guarded hot plate. The specimens are heated and cooled at a specified rate. The heating rate is reported and any cracking that may have occurred is described. Thermal spalling tests are designed to determine the resistance to thermal shock. An additional test (ASTM C1100), the Ribbon Thermal Shock Test, measures the elastic modulus and strength of aluminosilicate refractories before and after exposure to a thermal shock.

### 7.3. Special Tests

Even though the American Society for Testing and Materials offers a wide range of test methods, there are other special tests that are imposed upon the manufacturer by consumers, the military, the U.S. Government, and in some cases local or municipal governments. These tests are generally very specific and are oriented toward particular service conditions. In many instances, the producers develop special tests within their laboratories to solve customer problems or predict product or production performance. Many of these tests subsequently are adopted by ASTM.

## 8. Health and Safety Factors

Industrial refractories are by their very nature stable materials and usually do not constitute a physiological hazard. This is not so, however, for unusual refractories that might contain heavy metals or radioactive oxides, such as thoria and urania, or to binders or additives that may be toxic.

Inhalation of certain fine dusts may constitute a health hazard. For example, exposure to silica, asbestos, and beryllium oxide dusts over a period of time results in the potential risk of lung disease. OSHA regulations specify the allowable levels of exposure to ingestible and respirable materials. Material Safety Data Sheets, OSHA form 20, available from manufacturers, provide information about hazards, precautions, and storage pertinent to specific refractory products.

Manufacturers have recognized that products that exhibit a potential impact on the health and safety of users require greater sensitivity of handling. Safe use, disposal, and recycling of these products is the result. An example of such a product stewardship program is that developed by the refractory ceramic fiber (RFC) coalition. This program embraces the entire life cycle of the ceramic fiber products. The aim is to prevent unacceptable risks to those working with the fiber products. Similar programs are being developed in other refractory manufacturing segments.

## 9. Selection and Uses

Any manufacturing process requiring refractories depends on proper selection and installation. When selecting refractories, environmental conditions are evaluated first, then the functions to be served, and finally the expected length of service. All factors pertaining to the operation, service design, and construction of equipment must be related to the physical and chemical properties of the various classes of refractories (35).

Service conditions that impair effectiveness of refractories include chemical attack by, eg, slags, fumes, gases, etc; operating conditions, ie, temperatures and cycling; and mechanical forces, ie, abrasion, erosion, and physical impact. Design factors that influence selection include equipment type and construction, ie, brick or monolithic material; refractory function, ie, material containment, flow deflection, heat storage or release; heat environment, ie, exposure to constant or variable temperatures; refractory strength, ie, exposure to varying stress conditions; and thermal function, ie, insulation, dissipation, or transmission of heat.

The effects of processing conditions on refractories may be summarized as follows (35):

| Service condition | Chemical resistance |
|---|---|
| oxidizing atmosphere | oxides and combinations of oxides (ie, silicates, fireclays) are unaffected; carbon and graphite oxidize; silicon carbide is fairly stable to 1650°C |
| steam or water vapor | can cause hydration of magnesite refractories at low temperatures and oxidizes carbon and graphite above 705°C |
| hydrogen | silica and silica-containing refractories are attacked above 1100°C; high alumina, $ZrO_2$, MgO, and calcium–aluminate refractories show good resistance |
| sulfur and sulfates | above 870°C sulfur reacts with refractories containing silica; carbon and high purity oxides show good resistance; sulfates react to some degree; calcium–aluminate cement is more resistant than Portland cement |
| fuel ash | alkali and vanadium attack from ash can be severe on fireclay; high alumina resists |
| reducing atmosphere | most refractories are stable; however, iron oxide impurities, when reduced, can cause destruc-tion, particularly if cycled |
| carbon monoxide | iron impurities can act as a catalyst to cause deposition of carbon in fireclay refractories; CO can oxidize graphite and SiC and cause destructive changes in basic refractories |
| chlorine and fluorine | chlorine attacks silicates above 650°C; F attacks all refractory materials except graphite;basic refractories have poor resistance to both |
| acids | basic refractories have fair to poor resistance, fireclay and high alumina good resistance, except for HF; zircon, zirconia, and silicon carbide have good resistance; carbon and graphite do not react |
| alkalies | fireclay and high alumina perform well at low temperatures; magnesite refractories, fair to good; chrome refractories, poor; and graphite, excellent |

Standardized applications of different refractory types are listed in an excellent series compiled by the ASTM (36). These surveys cover the principal industrial applications of refractories and furnish a description of furnace operations and destructive influences such as slagging, erosion, abrasion, spalling, and load deformation.

By far the most common industrial refractories are those composed of single or mixed oxides of Al, Ca, Cr, Mg, Si, and Zr (see Tables 1, 4, and 6). These oxides exhibit relatively high degrees of stability under both reducing and oxidizing conditions. Carbon, graphite, and silicon carbide have been used both alone and in combination with the oxides. Refractories made from these materials are used in ton-lot quantities, whereas silicides are used in relatively small quantities for specialty application in the nuclear, electronic, and aerospace industries.

The common industrial refractories are classified into acid, $SiO_2$ and $ZrO_2$; basic, CaO and MgO; and neutral, $Al_2O_3$ and $Cr_2O_3$. Oxides within each group are generally compatible with each other, whereas mixtures of acid and basic oxides often give low melting products. Neutral oxides are generally compatible with both acidic and basic oxides.

### 9.1. Reactions Between Refractories and Liquids

Molten metals are generally much less reactive than slags. Therefore, the response of a refractory to a chemical environment generally depends on its slag resistance which, in turn, depends on the compositions and properties of slag and refractory. Other factors include temperature, severity of thermal cycling or shock of the process, velocity and agitation of the slag in contact with the refractory, and the abrasion to which the refractory is subjected. Considering these factors, it is not surprising that similar refractories placed in similar furnaces can wear at vastly different rates under different operation practices.

The basicity of slags and refractories is determined by the ratio of the basic oxides to acid oxides. Most often this ratio is taken to be the ratio of the lime to silica, ie, the most influential basic and acid oxides, respectively. More complex formulas are commonly used, however. As a general rule, acid slags ($CaO/SiO_2$ $<1$) require acid refractories (see Table 4); basic slags ($CaO/SiO_2$ $>1$) require basic refractories (see Table 6). Fireclay and aluminosilicate refractories perform best for slags having a $CaO/SiO_2$ ratio $<1$; however, for acid slags containing considerable amounts of iron or manganese oxides, high alumina refractories are required. High alumina refractories are also superior to fireclay refractories when the $\text{basicity} - \text{to} - \text{acidity ratio} = 1$. When the $CaO/SiO_2$ ratio $> 1$, basic refractories such as MgO, MgO–CaO, and MgO–$Cr_2O_3$ should be employed. Magnesium oxide resists slags of a wide range of compositions; however, in actual practice all basic refractories contain some silica which usually occurs in various silicate phases at the grain boundaries.

As slag attack proceeds, liquid phases migrate from the hot face to the cooler regions and attack of the grain-boundary silicate phase precedes solution of the periclase grain. For this reason, both the character of the bonding silicate phase and the porosity of the refractory are important. Penetration of the slag may be impeded by materials such as carbon, pitch, or resins by lowering the porosity and changing the wetting characteristics.

Slags penetrate refractories until the viscosity becomes too high for further migration. Refractories having high thermal conductivity can cause the slag to chill and thus the penetrated volume is reduced. High thermal gradients within a refractory often reduce the effect of slag. Therefore, efforts to increase the thermal conductivity of refractories and create high thermal gradients to refractories exposed to high slag conditions have been made. Use of internal metal plates within refractories have been tried. Incorporating large flake graphite in the magnesium oxide refractories is common. The success of this approach has led to the use of flake graphite in other oxide systems including alumina and spinel. Using water-cooled panels behind these high thermal conductivity refractories to increase the thermal gradient has also been tried. The technique was so successful that water cooling panels without refractories are common in electric furnaces above slag lines.

Slag penetration alters the structure of the refractory by changing its porosity, density, mineralogical makeup, and strength. If the altered refractories are subject to thermal cycling or if volume changes occur upon crystallization of the slag, stress concentrations build up immediately behind the densified zone and spalling or cracking may result. An example of structural alternation is the iron oxide bursting phenomenon in magnesite–chromite brick. Iron oxide contained in the chromite ore, or that which is allowed to penetrate the brick, can cause excessive expansion of the lattice because of the unequal diffusion of the iron and chromium ions in magnesia chrome spinel, which leads to the production of pores in the iron-brick phase.

### 9.2. Reactions Between Refractories and Gases

Reactions of refractories and gases can be quite destructive. The gases generally penetrate the pores of the refractory destroying its structure. The refractory may either expand and crack because of the formation of new, low density compounds, or its refractoriness may be drastically reduced because low melting compounds are formed. An example is the disintegration of aluminosilicates in blast furnaces caused by carbon monoxide. The deposition of carbon is catalyzed by iron in the bricks. The growth of the carbon deposit causes the brick to rupture and more surface is exposed. Therefore, a brick of low iron and alkali content having a dense, low permeability is preferred.

### 9.3. Reactions Between Refractories

In Table 17, the compatibilities of various refractories are given over a range of temperatures. Dissimilar refractories can react vigorously with each other at high temperatures. Phase diagrams are an excellent source of information concerning the reactivity between refractories.

**Table 17. Approximate Initial Temperature, °C, at which Refractories React$^{a, b}$**

| Refractory | Magnesite, 92% MgO | Magnesite–chrome, CB$^c$ | Chrome–magnesite CB$^c$ | Chrome–magnesite Fired | Forsterite, stabilized | Chrome, fired | Alumina 90% | Alumina 70% |
|---|---|---|---|---|---|---|---|---|
| magnesite, 92% MgO | | >1700 | >1700 | >1700 | (1700) | 1700 | >1700 | 1600 |
| magnesite–chrome, CB$^c$ | >1700 | | >1700 | >1700 | 1650 | >1700 | 1450 | 1450 |
| chrome–magnesite | | | | | | | | |
| CB$^c$ | >1700 | >1700 | | >1700 | 1650 | >1700 | 1650 | 1600 |
| fired | >1700 | >1700 | >1700 | | 1650 | >1700 | 1650 | 1650 |
| forsterite, stabilized | (1700) | 1650 | 1650 | 1650 | | 1650 | 1650 | 1600 |
| chrome refractories, fired | 1700 | >1700 | >1700 | >1700 | 1650 | | 1650 | 1600 |
| alumina | | | | | | | | |
| 90% | >1700 | 1600 | 1600 | 1600 | 1650 | 1650 | | >1700 |
| 70% | 1650 | 1600 | 1600 | 1500 | 1650 | 1600 | >1700 | |
| zircon | >1700 | 1600 | 1650 | 1600 | 1600 | >1700 | >1700 | >1700 |
| fireclay | | | | | | | | |
| superduty | 1400 | (1700) | 1650 | 1650 | 1600 | 1500 | (1700) | (1700) |
| high duty | 1400 | 1650 | 1600 | 1600 | 1650 | 1500 | (1700) | (1700) |
| semisilica | 1500 | 1400 | 1400 | 1500 | 1500 | 1500 | (1500) | (1500) |
| silicon carbide, clay-bonded | 1500 | 1400 | 1400 | 1400 | 1600 | 1500 | 1650 | 1650 |
| silica | | | | | | | | |
| type B$^d$ | 1500 | 1600 | 1600 | 1500 | 1650 | 1650 | 1650 | 1500 |
| superduty | 1500 | 1600 | 1600 | 1600 | 1650 | 1650 | 1650 | 1500 |

[a] Ref. 26; values in parentheses are estimated.

[b] Max temperature tested = 1700°C.

[c] CB = chemically bonded (not fired); one or both materials not sufficiently refractory for test.

[d] Ref. 34.

### 9.4. Silica Refractories

This type consists mainly of silica in three crystalline forms: cristobalite [14464-46-1], tridymite [1546-32-3], and quartz [14808-60-7]. Quartzite sands and silica gravels are the main raw materials, although lime and iron oxides are added to increase the mineralization of the tridymite and cristobalite. Uses include roof linings, refractories for coke ovens, coreless induction foundry furnaces, and fused-silica technical ceramic products. Consumption of silica refractories has declined dramatically since the 1960s as a result of the changes in the steel industry.

### 9.5. Fireclay Refractories

These products are made from clay minerals containing ca 17–45% $Al_2O_3$. Pure kaolin has the highest alumina content. Fireclay refractories are used in kilns, ladles, and heat regenerators, acid–slag-resistant applications, boilers, blast furnaces, and rotary kilns. They are generally inexpensive.

### 9.6. High Alumina Refractories

The desired alumina content, from 100% to just above 45%, is obtained by adding bauxites, synthetic aluminosilicates, and synthetic aluminas to clay and other bonding agents. These refractories are used in kilns, ladles, and furnaces that operate at temperatures or under conditions for which fireclay refractories are not suited.

Phosphate-bonded alumina bricks have exceptionally high strength at low to intermediate temperatures and are employed in aluminum furnaces. High alumina and mullite are used in furnace roofs and petrochemical applications.

### 9.7. Chrome Refractories

Naturally occurring chrome ore composed mainly of chromite [53293-42-8] may be made into a brick or blended with fine calcined magnesite to obtain the desired chrome-to-magnesia ratio. When blended with magnesite, the products containing more chrome than magnesia are denoted chrome magnesite. These refractories are used in nonferrous metallurgical furnaces, rotary kiln linings, and secondary refining vessels, such as argon–oxygen decarborizers (AODs) and glass-tank regenerators. Chrome and alumina are isomorphous and form a complete series of solid solutions. Small amounts of chrome in alumina increase the resistance to metal penetration dramatically.

### 9.8. Magnesite Refractories

These refractories do not contain magnesite as their name implies, but rather periclase. The term magnesite refers to the ore from which the periclase was made, although magnesite brick can be made from synthetic periclase, ie, seawater MgO. Shaped magnesite refractories may be impregnated or bonded with pitch or resin to improve resistance to slag attack. Chrome ore can be added to magnesite to produce magnesite–chrome refractories used in lining and maintenance of steelmaking and refining vessels and checkers.

### 9.9. Dolomite Refractories

Refractories containing dead-burned dolomite and possibly fluxes such as millscale, serpentine, or clay are dolomite refractories. Shaped refractories may be bonded or impregnated with pitch to improve slag resistance and inhibit hydration. Addition of magnesite gives magnesite–dolomite (magdol) refractories. Dolomite refractories are primarily used in linings of BOF vessels and refining vessels, and in ladles and cement kilns.

### 9.10. Spinel Refractories

These refractories, which contain synthetic spinel, $MgAl_2O_4$, exhibit good strength at high temperatures as well as thermal shock resistance. Chromium and magnesium oxides crystallize in the same structure and are referred to as chrome–magnesite spinels. Spinel refractories have been used in cement kilns, AOD vessels, and steel-ladle linings.

### 9.11. Forsterite Refractories

Refractories made from forsterite, $Mg_2SiO_4$, resist alkali attack and have good volume stability, high temperature strength, and fair resistance to basic slags. Uses include nonferrous metal furnace roofs and glass-tank refractories not in contact with the melt, ie, checkers, ports, and uptakes.

### 9.12. Silicon Carbide Refractories

Silicon carbide has a wide range of refractory uses including chemical tanks and drains, kiln furniture, abrasion-resistant linings, blast-furnace linings, and nonferrous metallurgical crucibles and furnace linings. These materials are also used in power plant cyclone boilers and in municipal/waste-to-energy incineration (see Incinerators; Power generation).

### 9.13. Zirconia Refractories

The most common zirconia-containing refractories are made from zircon sand and are used mostly for container glass-tank subpaver brick. Refractory blocks made from a composition of zircon and alumina, used to contain glass melts, are generally electromelted and then cast. These exhibit excellent corrosion resistance but are subject to thermal shock. Refractories made from pure $ZrO_2$ are extremely expensive and are reserved for extra high temperature service above 1900°C. Additives such as yttria or CaO and MgO prevent deterioration during heating and cooling.

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