12.0 Background

Refractories are material having high melting points, with properties that make them suitable to act as heat-resisting barriers between high and low temperature zones. Refractories are useful in constructing application-specific high temperature areas/surfaces, particularly in furnaces or boilers, as they minimize heat losses through structure.

The value of refractories is judged not merely by the cost of the material itself, but by the nature of job and/or its performance in a particular situation. Specifically, the performance of a refractory depends on its qualities and quantities in three phases—solid, glass/liquid, and pores—which govern the ultimate property of a refractory material.

A ‘green bond’ is developed by mixing various sizes of similar refractory material having some strength and property, which are changed during firing/heat treatment in the course of service. The qualities of refractories are thus dependent on their chemical, physical, mineralogical and thermal properties.

Refractory materials are generally tailor-made on the basis of:
  - Process parameters like temperature profile, mode of operation, chemical environment, etc.
  - Expected quality characteristics
  - Best techniques for engineering and application, so that the final physical, chemical, mechanical, and thermal properties are compatible to the application

Refractory materials are used in two different forms, namely, shaped and unshaped products.

12.1 Shaped refractories

The most familiar form of refractory materials is the rectangular brick shape. However, refractories are presently available in a variety of shapes and sizes for convenience in construction.
12.2 Unshaped refractories

There is a class of refractory materials which can form joint-less lining. This class of refractory materials is called monolithic. All unshaped refractory materials have this ability to form joint-less lining, and hence they are grouped as monolithic.

- Unshaped refractories are manufactured in powder form as granular material and known as castables, ramming masses, gunning mix, plastic masses, etc.
- Castables are mixed with water before casting.
- Ramming masses are first mixed with water or any other liquid to the required quality, and then rammed either manually or pneumatically with a heavy rammer.
- Gunning masses are passed through a machine in which the powder material is put under pressure and conveyed pneumatically through a hose. The material gets mixed up with water before it exits the hose nozzle, and sticks to the surface on which it is applied to form a lining.
- Plastic masses comprise ready-mix material that is applied manually in the furnace to form a lining.

12.3 Classification

The primary constituents of any refractory may be a single compound like alumina, silica or mullite, or a combination of these materials. Their melting points are as follows:

- Silica (SiO₂) – 1723 °C
- Alumina (Al₂O₃) – 2050 °C
- Mullite (71.8% Al₂O₃, 28.2% SiO₂) – 1996 °C

Relatively small amounts of oxides of sodium (Na₂O) and potassium (K₂O), and other minerals containing calcium (CaO), magnesium (MgO), titanium (TiO₂), and iron oxide, promote liquid-phase formation at low temperatures. Hence, the presence of these oxides in refractories must be limited to trace amounts to avoid formation of low temperature liquid phase.

Refractories in which the predominant constituents are alumina, silica or a combination thereof may be placed in the following categories:

- Fireclay refractory
- High alumina refractory
- Silica refractory
- Mullite refractory

12.3.1 Fireclay refractory

Fireclays are hydrated aluminum silicates that occur naturally. They are sufficiently pure to serve as raw materials for refractories. The principal mineral in fireclays is kaolinite. While other clay minerals may be present, the formula Al₂O₃·2SiO₂·2H₂O can usually represent the clay fraction. As
kaolinite is heated to high temperatures when used to make refractories, it loses its water; theoretically, 45.9% alumina and 54.1% silica remain.

Plastic and semi-plastic fireclays, as their names indicate, develop varying degrees of plasticity when they are mixed with water. This is an important factor in the manufacture of fireclay bricks, because the plastic fireclays facilitate the forming process and act as a bonding phase for the raw and calcined flint clays, and they have greater variation in their impurity content.

12.3.2 Silica refractories

Silica bricks are made from raw materials that are essentially quartz. During the initial firing, alpha-quartz is first converted to beta-quartz, accompanied by an abrupt expansion at 573 °C. Slow rates of heating are required through this temperature range to prevent cracking, as the volume change is about 0.9%. Since the final firing temperature is somewhat over 1426 °C, the brick as it is put into service consists of cristobalite particles (properties of cristobalite are not affected by temperature fluctuation, provided the temperature does not drop below 600 °C), with possibly some having residual unconverted quartz cores.

12.3.3 High-alumina refractories

High-alumina bricks serve as a multi-purpose refractory material for severe environments. They are used extensively in the steel industry for such applications as hot metal cars, electric furnace roofs, piers and muffles for a variety of furnaces, and numerous applications where strength at high temperature is an essential requirement. The aluminium and glass industries use high-alumina refractories to keep the melt in the molten state.

Most high-alumina refractories are classified according to their alumina content, which could range from 50%–99%. They are designated as 50%, 60%, 70%, 80%, 85% and 90% alumina. Two classes of high-alumina refractories are distinguished by a microstructure that is essentially a single, crystalline phase. These are: (1) mullite refractories and (2) corundum refractories.

12.3.3.1 Mullite refractories

Mullite is about 72% alumina with 28% silica. The manufacturing procedures are designed to maximize the formation of the compound mullite (3Al₂O₃·2SiO₂). A refractory with 71.8% alumina and 28.2% silica will be composed of only mullite (3Al₂O₃·2SiO₂) if fired at equilibrium conditions. However, the extent to which well-developed mullite crystalline form occurs in a refractory depends on the purity of the raw
materials used and the manufacturing processes, particularly firing. Therefore, all high-alumina bricks with around 70% alumina may have a well-developed mullite phase. Mullite refractories have excellent volume stability and strength at high temperatures. They are highly suitable material for electric furnace roofs, blast furnaces and blast furnace stoves, hot metal cars, and the superstructure of glass tank furnaces.

12.3.3.2 Corundum refractories

The 99% alumina class of refractories is called corundum. These refractories comprise single-phase, polycrystalline, alpha-alumina.

### 12.4 Properties of refractory materials

The quality of a refractory and its suitability for a particular application primarily depends on its physical, chemical and mineralogical properties. It may be possible to assess the quality of a refractory on the basis of a single property or a group of properties. The most common properties that are considered in selecting the optimum refractory lining configuration are listed below.

1. Apparent porosity
2. Bulk density
3. Modulus of rupture (MOR)
4. Hot modulus of rupture (HMOR)
5. Cold crushing strength
6. Pyrometric cone equivalent (PCE)
7. Thermal expansion
8. Thermal expansion under load (TEUL) and creep
9. Thermal conductivity

Both shaped and unshaped refractories are available in the market under different brand names with special features and for different applications. The analytical data on these products are generally provided in the company product brochures. However, purchasers are advised to get refractory samples analysed once in a while to verify/cross check the supplier’s claims as well as assess the quality of the procured refractory on their characteristics, consistency and variation in composition due to imperfect manufacturing.

12.4.1 Apparent porosity

The apparent porosity is a measure of the effective open pore space in a refractory into which molten metal, slag, fluxes, vapours, etc. can penetrate and thereby contribute to eventual degradation of the structure. The porosity of any product is expressed as the average percentage of open pore space in the overall refractory volume.
12.4.2 Bulk density

The bulk density is generally considered in conjunction with apparent porosity. It is a measure of the weight of a given volume of refractory. For many refractories, the bulk density provides a general indication of the product quality. While evaluating a refractory brand or comparing several products of equivalent type (except insulating types), it is considered that the refractory with higher bulk density (generally concurrent with lower porosity) will be better in quality. The structure of a refractory having higher bulk density will be denser, resulting in better resistance to chemical attack, decreased metal penetration, better abrasion resistance and other related benefits.

12.4.3 Modulus of rupture (MOR)

The modulus of rupture (MOR) is the flexural breaking strength of a refractory. MOR is measured at room temperature and expressed in pounds per square inch or kilograms per square centimeter.

12.4.4 Hot modulus of rupture (HMOR)

The hot modulus of rupture (HMOR) is the flexural breaking strength of a refractory at a chosen elevated temperature or over a range of temperatures. The structural integrity and general abrasion characteristics of a refractory can be estimated from HMOR, making it an essential property to determine the suitability of a refractory in a certain temperature profile for a certain set of application conditions.

12.4.5 Cold crushing strength

The cold crushing strength is the capacity of a refractory to provide resistance to a compressive load at room temperature. It is the load, in pounds per square inch or kilograms per square centimeter, at which the refractory breaks.

12.4.6 Pyrometric cone equivalent (PCE)

The pyrometric cone equivalent (PCE) is a measure of the refractoriness and state of maturity of the material composition of a refractory product after firing. It represents the state at which a refractory mixture/composition starts becoming soft and deforms within a particular temperature range, depending upon the heating pattern in the firing stage.

Representative PCE values for selected refractories include cones 33–34 for super duty fireclay, cones 29–31 for medium duty fireclay and cones 36–37 for a 60% alumina product. The cone values reported for refractories are based on a defined standard time–temperature relationship, so different heating rates will result in different PCE values. PCE can be useful for quality control purposes to detect variations in batch chemistry.
that result from changes or errors in the raw material formulation.

12.4.7 Thermal expansion
Thermal expansion is the intrinsic characteristic of refractory products to expand on heating and contract on cooling. The dimensional changes of a refractory due to thermal expansion are commonly expressed in permanent linear change (%) and the coefficient of thermal expansion (length per unit length).

12.4.8 Thermal expansion under load (TEUL) and creep
Dimensional changes take place in a refractory under a compressive load at elevated temperature. The dimensional change could be linear on increasing the temperature, which is known as thermal expansion under load (TEUL). The dimensional changes due to extended period of holding/soaking of a refractory at pre-selected temperature is nonlinear, and leads to plastic deformation known as creep. More specifically, creep is the heat-activated plastic deformation of a body under stress as a function of time. TEUL and creep are typically determined in sequence in the same test, using the same sample.

12.4.9 Thermal conductivity
The thermal conductivity is defined as the quantity of heat that will flow through a unit area in a direction normal to the surface area in a defined time with a known temperature gradient under steady state conditions across the area. It indicates the general heat flow characteristics of refractories. The heat flow potential is higher with higher thermal conductivity value, and vice versa. High thermal conductivity refractories are required for some applications where good heat transfer is essential, such as coke oven walls, regenerators, muffles, and water-cooled furnace walls. However, refractories with lower thermal conductivity are preferred in industrial applications, as they help in conserving heat energy.

The thermal conductivity of refractories is dependent on factors such as chemical and mineralogical composition, temperature, porosity, extent of sintering, and furnace environment. Porosity is a significant factor in heat flow through refractories. The thermal conductivity of a refractory decreases on increasing its porosity.

12.5 Quality assessment of refractory materials
The critical properties of a refractory should be analysed for generic assessment of its quality, and to compare the analytical results with the quantitative values of the properties of the refractory that are supplied by the manufacturer.
12.5.1 Physical analysis

All refractory materials contain pores of varying quantity. The majority of the physical properties, that is, density, strength, expansion, and thermal conductivity of materials, are directly influenced by the quantity and quality of these pores. Two types of pores—closed and open—are observed in a refractory. Pores which do not have any connection with the atmosphere are known as closed pores, while those that have access to the atmosphere are known as open pores. These are normally expressed in terms of percentage of total volume and could be calculated from the mass and volume of any refractory material. The mass of a refractory could be measured either in solid state ($W_{ss}$) or in powder state ($W_{ps}$). Similarly, its volume too could be measured either in solid state ($V_{ss}$), which includes the volume of pores, or in powder state ($V_{ps}$), which does not include the volume of pores. It is also possible to measure the volume of pores ($V_{pore}$) present in a solid state of refractory material.

By analysing porosity alone, it is possible to assess refractory quality. Porosity is defined as the ratio of volume of vacant spaces/pores ($V_{pore}$) to the total volume of material ($V_{ss}$) expressed in percentage.

Therefore, porosity (%) = $V_{pore} / V_{ss}$ in percentage.

Specific or true density is defined as the ratio of the weight of the material in powder state ($W_{ps}$) to its volume ($V_{ps}$) in the same state. The material is powdered to some definite size so that there are no pores available in the material.

Therefore, true density (TD, in grams/cubic centimetre) = mass ($W_{ps}$) in grams/volume of solid ($V_{ps}$) in cm$^3$.

Bulk density (BD) is determined for refractory material having open and closed pores. It is the ratio of mass in solid state ($W_{ss}$) to bulk volume ($V_{ss}$) of a refractory.

Thereafter, the volume of open pores can be found out by some easy method (for instance, by filling the open pore areas with water or other liquid and measuring the volume of water/liquid, which gives the volume of open pores) to calculate the apparent density (AD) of the refractory. The apparent density (AD) is defined as the ratio of mass in solid state ($W_{ss}$) to the resultant volume, which is obtained by adding the volume of solid ($V_{ss}$) with the volume of closed pores ($V_{pore}$). AD is expressed in grams/ cubic centimetre.

Therefore, AD = $W_{ss} / (V_{ss} + V_{pore})$ grams/ cm$^3$

The quantities of total pores, open pores and closed pores can be determined using three density data: i.e., true density, bulk
density, and apparent density. These values for any refractory could be easily obtained and are necessary for assessing its quality and expected performance.

12.5.2 Chemical and mineralogical analysis
Refractories are identified by their major chemical constituents, which govern their quality and properties. It is essential to carry out complete chemical analysis of refractory materials for its quality assessment. As a thumb rule, it is known that the higher the alumina content, the better is the property. However, it is obvious that while the major chemical constituents of a refractory do play the most important role in determining its ability to perform, the minor constituents—mainly impurities—also play a very important role in its performance.

Refractory materials are normally oxides having a tendency to react with one another at high temperature to form different compounds with different crystal structures. The mineralogical formation and crystal structures of the same chemical constituents will vary depending upon the extent of heat treatment/thermal exposure the material receives in manufacturing or in operating conditions. The crystal structure that forms will decide the performance of the refractory, as the resistance to corrosion/erosion behaviour largely depends on it. Therefore, it is essential to know the microstructure of the refractory along with its chemical constituents.

Quality assessment could be carried out of the refractory material by analysing randomly selected samples from the lot for complete chemical composition, apparent porosity, bulk density, apparent density, HMOR, and mullite content. However, estimation of mullite percentage will require X-Ray analysis, for which facilities are not available everywhere. Hence, mullite percentage has to be estimated from other physical tests, and an occasional check of this parameter will suffice.

12.6 Refractory for pot furnace lining
Construction of a furnace would require the use of different types of refractories, each suitting the temperature profile of a particular area. The details of the refractory materials used in open pot furnace construction are shown in Table 12.1.

Table 12.1: Details of refractories used in open pot furnace

<table>
<thead>
<tr>
<th>Refractory type</th>
<th>Application area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red bricks</td>
<td>Level foundation, tri area, chimney base and outer sides of the flue paths</td>
</tr>
<tr>
<td>IS-6 bricks</td>
<td>Flue path area after recuperator</td>
</tr>
<tr>
<td>IS-8 bricks</td>
<td>Crown, flue path area</td>
</tr>
<tr>
<td>Silica bricks</td>
<td>Crown and furnace wall between pillars</td>
</tr>
</tbody>
</table>
Red bricks, IS-6 bricks and IS-8 bricks are all fireclay refractory bricks whose standards are already outlined by the BIS (Bureau of Indian Standards) covering standard dimensions, physical and chemical properties.

12.6.1 Sillimanite block

The term ‘Sillimanite’ is in fact a misnomer. Sillimanite generally represents a high-alumina refractory with a higher percentage of mullite. High-alumina refractories are particularly suitable for high-temperature applications (such as in the open-pot furnace for glass melting), with typical process parameters like thermal stress and chemical environment. High-alumina refractories having the following characteristics are suitable for furnace floor construction:

- High temperature resistance (at least up to 1450 °C)
- High corrosion resistance (alkali resistant)
- Resistance to thermal fluctuation

Table 12.2 shows detailed physical and chemical properties of Sillimanite refractories.

### Table 12.2: Properties of Sillimanite refractories

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3</td>
<td>≥ 60% minimum (preferably around 70%)</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>≤ 0.5% maximum</td>
</tr>
<tr>
<td>PLC (at 1500 °C)</td>
<td>± 0.2%</td>
</tr>
<tr>
<td>Apparent porosity</td>
<td>15%–17%</td>
</tr>
<tr>
<td>Cold crushing strength</td>
<td>≥ 400 kg/cm² minimum</td>
</tr>
<tr>
<td>Bulk density</td>
<td>≥ 2.50 g/cc minimum</td>
</tr>
<tr>
<td>RUL</td>
<td>1580 °C</td>
</tr>
<tr>
<td>HMOR (1400 °C)</td>
<td>≥ 60–65 kg/cm² minimum</td>
</tr>
<tr>
<td>Mullite</td>
<td>≥ 50% minimum (indicative)</td>
</tr>
<tr>
<td>Notes:</td>
<td>PLC—permanent linear change</td>
</tr>
<tr>
<td>RUL—refractoriness under load</td>
<td></td>
</tr>
</tbody>
</table>

12.7 Improving operating life of the furnace lining

The following practices may be observed while carrying out furnace lining, in order to ensure longer operating life of the furnace. The process begins with procurement of appropriate, good quality refractory material.
12.7.1 Consistent quality
The quality of the refractories used in pot furnace floor needs to be consistent and assured. Blocks are to be procured from reputed manufacturers, as the quality of such blocks can be expected to be uniform. Normally, reputed manufacturers have the requisite infrastructure and relevant manufacturing know-how for developing the correct physical properties in the blocks such as strength at high temperature (HMOR), and correct mineralogy (mullite content). Once these desired properties are achieved during the manufacturing process, the performance of the refractory material will be predictable and better.

12.7.2 Using larger refractory blocks
The use of larger blocks reduces the number of joints while constructing a furnace lining. However, this does not always result in improvement of performance. The manufacturing of large blocks requires a high-capacity press for developing uniform property characteristics. Hence, it is necessary to consider the dimensions of the block vis-à-vis its properties (from the suppliers' product brochure) to ensure its suitability for a particular application. Further, random samples from the procured lots should be analysed to verify the manufacturer's claims with the results obtained from sample analyses.

12.7.3 Mortar quality
The qualities of mortar used in furnace lining should be similar to the refractory qualities /properties. Low shrinkage (less than 1%) high-alumina mortar should be used for joining the high-alumina blocks.

12.7.4 Proper dimension
Dimensionally accurate and warpage-free blocks should be used in furnace lining.

12.7.5 Use of anticorrosive coating
The floor of the furnace is likely to be damaged due to the spillage of charge materials containing alkalis or due to contact with molten glass in case of pot failure. In general, it has been found that sparking and corrosion are the main causes of wear and tear of refractories in industrial processes. The glass industry is no exception. Bricks with resistance to sparking and corrosion are preferable for using on the floor of the glass melting furnace. Anti-corrosive coating materials particularly suitable for alkali attack could be considered. The coating should be uniform, and may be 5 mm thick.