Ceramics & Refractories

> *"Character, like porcelain ware, must be printed before it is glazed. There can be no change after it is burned in."*

1 INTRODUCTION

The word *ceramics* is derived from Greek word "Keramos" which means burnt stuff. Products made from natural earths that had been exposed to high temperatures were earlier called as ceramics. Now a days *ceramics* are defined as inorganic, non-metallic materials that are processed and/or used at high temperatures. Most ceramic materials contain silicates, metallic oxides and their combinations.

The important types of ceramic materials, their properties and applications are summarized below in Table 1.

Table 1.

	Ceramic Material	*Properties*	*Applications*
1.	Carborundum, Boron nitride	Hardness and Resistance to wear	Grinding and cutting wheel
2.	Cement, brick	Much higher compressive strength than tensile strength	Cement and brick are preferably used in compression than in tension
3.	Barium titanate and modified lead zirconate titanate	Piezoelectric property [property of transforming mechanical deformations into voltage changes and vice-versa]	Gramophone pick-ups, Roughness meters
4.	Magnesia, Zirconia, Porcelain, alumina etc.	Very good chemical resistance even at very high temperatures	Crucible and furnace linings
5.	Glazed porcelain	Excellent chemical resistance	Chemical vessels
6.	Glasses	Refractive index easily variable	Manufacture of lens
7.	Ferrites	High resistivity and magnetic properties	Electronic applications
8.	Refractories	Excellent chemical, heat and Abrasion resistance	Furnace walls and roofs, ladles for pouring metal into mould etc.

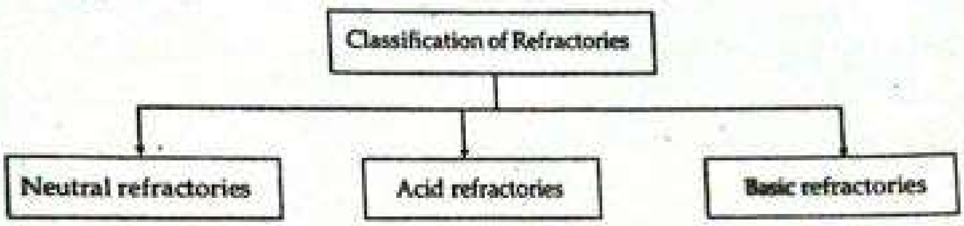
The existence of many ceramic materials with quite different properties is due to the fact that many combinations of the metallic and non-metallic atoms, with several structural arrangements for each combination, are possible. The constituents of ceramic material may form covalent or ionic bonds. Most of the ceramics are insulators like other covalent materials. They are highly stable and have high melting points which indicate that there exists ionic bonding as well in them.

2 REFRACTORIES

Refractories are ceramic materials that can withstand high temperatures as well as abrasive and corrosive action of molten metals, slags and gases, without suffering a deformation in shape. The main objective of a refractory is to confine heat.

Classification of Refractories

On the basis of the chemical properties of their constituent substances, refractories are classified into three categories :



(*a*) *Neutral refractories* like graphite, zirconia and SiC (carborundum) refractories. These refractories are made from weakly basic/acidic materials like carbon, zirconia (ZrO_2) and chromite ($FeO.CrO_2$)

(*b*) *Acid refractories* like alumina, silica and fire clay refractories. These refractories consist of acidic materials like alumina (Al_2O_3) and silica (SiO_2). These refractory materials are resistant to acid slags (like silica) and are often used as containment vessel for them. On the other hand, they are readily attacked by basic slags (like CaO, MgO etc.) and contact with these oxide materials should be avoided.

(*c*) *Basic refractories* like magnesite and dolomite refractories. These refractories consist of basic materials like CaO, MgO etc. and are especially resistant to basic slags. That's why they find extensive use in some steel making open hearth furnaces. The presence of acidic materials like silica is deleterious to their high-temperature performance.

Characteristics of refractory materials

(*i*) A good refractory material should have excellent heat, corrosion and abrasion resistance ;

(*ii*) It should possess low thermal coefficient of expansion and should expand and contract uniformly, with increase and decrease of temperature respectively ;

(*iii*) It should possess high fusion temperature. It should be infusible at the temperature to which it is liable to be exposed ;

(*iv*) It should be able to withstand the overlying load of structure, at operating temperatures.

(*v*) They should be chemically inert towards corrosive action of molten metal, gases and slags, produced in its immediate contact in furnaces.

(*vi*) They should not crack at the operating temperatures.

If a given refractory material does not have the above mentioned characteristics, it will fail in service. Thus, we can easily summarize ***conditions which lead to failure of a refractory material as*** :

(*i*) Using a refractory material which do not have required heat, corrosion and abrasion resistance ;

(*ii*) Using refractory material of higher thermal expansion ;

(*iii*) Using a refractory of refractoriness less than that of the operating temperature ;

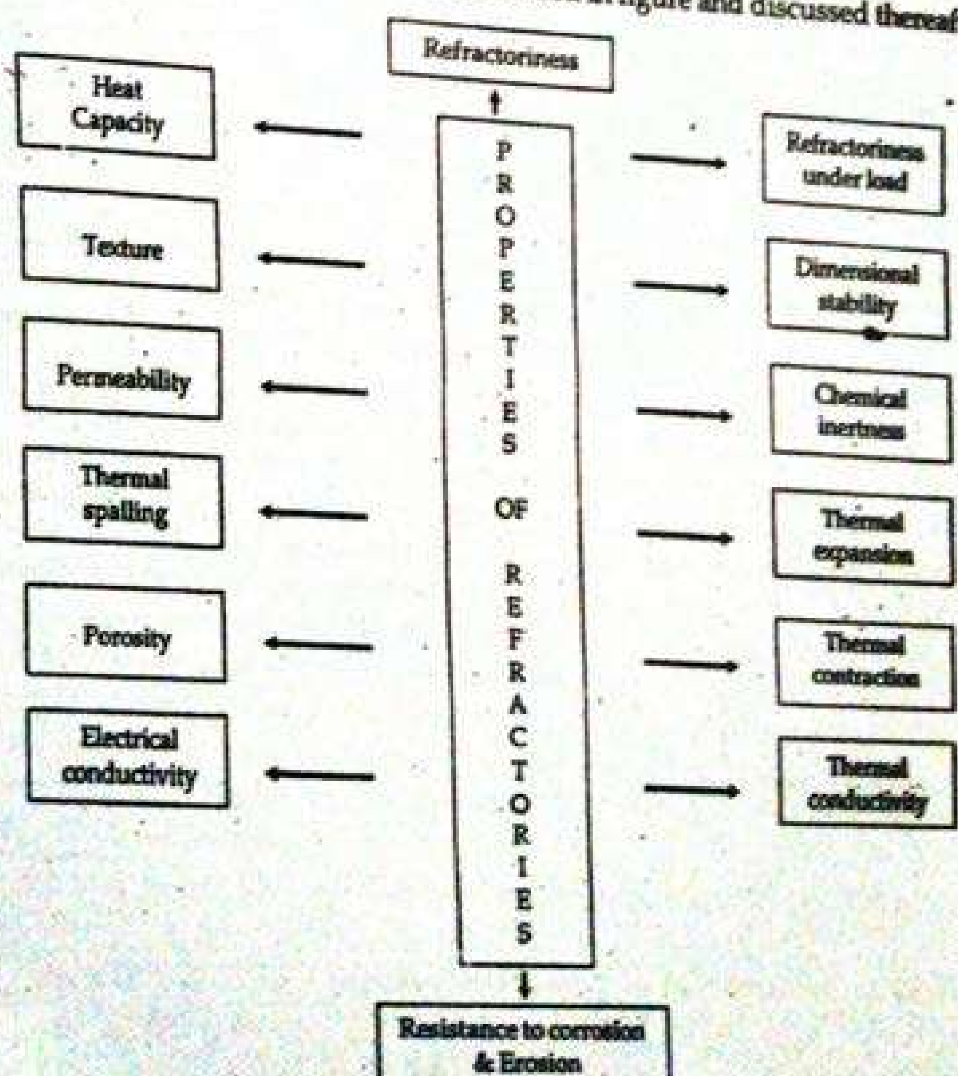
(*iv*) Using lower-duty refractory bricks in a furnace than the actual load of raw materials in products ;

(*v*) Using basic refractory in a furnace in which acidic reactants and/or products are being processed and vice-versa ;

(*vi*) Using refractories which undergo considerable volume changes during their use at high temperature.

3 PROPERTIES OF REFRACTORIES

The important properties are summarized in figure and discussed thereafter :



(a) **Refractoriness.** *"It is the ability of a refractory material to withstand the heat without appreciable softening or deformation under given service conditions."* It is generally measured as the softening temperature. It is necessary that a refractory material should have a softening temperature higher than the operating temperature of the furnace in which it is to be used. Sometimes, it can be employed to withstand a temperature higher than its softening temperature since the outer part of refractory is at a lower temperature and still in solid state, providing strength. Thus, refractory material does not melt away although inner refractory lining in a furnace is at a much higher temperature than the outer ones. Most of the commercial refractories do not exhibit sharp melting points and they soften gradually over a range of temperatures. This is due to the fact that they are composed of several minerals, both crystalline and amorphous in nature. Fusion temperatures of some neutral, acidic and basic refractories are given in Table 2.

Table 2 : *Fusion Temperatures of Neutral, Acidic and Basic refractories*

S.No.	Refractory type	Refractory material	Fusion temperature (°C)
1.	Neutral	Graphite (C)	3500
2.	Neutral	Zirconia (ZrO_2)	2710
3.	Neutral	Silicon carbide (SiC)	2700
4.	Acidic	Alumina (Al_2O_3)	2050
5.	Acidic	Silica brick (SiO_2)	1700
6.	Acidic	Fire clay brick	1600-1750
7.	Basic	Magnesia brick	2200

Measurement of Refractoriness. The softening temperatures of refractories are generally determined by ***seger cones (also called pyrometric cones) test.*** In this test, behaviour of heat on cone of refractory (to be tested) and series of seger cones of standard dimensions are compared. These cones are small pyramid shaped with triangular base, 38 mm high with 19 mm long sides. The test refractory in the form of a cone is kept along side similar sized standard cones and all are heated uniformly at 20°C/hr or 100°C/hr or 150°C/hr or occasionally at 600°C/hr. As seger cones are made of a particular refractory of a definite softening temperature so they are assigned ascending seger cone numbers with increasing softening temperature. When the test cone softens and loses its shape, one of the standard seger cone also softens and loses its shape provided its refractoriness is close to that of the test cone. The serial number of this standard seger cone is noted and this number is the *Pyrometric cone equivalent* (PCE) of the refractory under that test. When the test cone softens earlier than one standard cone, but later than the previous one, the PCE value of the test sample is approximated as average of the two.

The temperature at which the softening or fusion of the test-cone occurs is indicated by its apex touching the base, see Fig. 1.

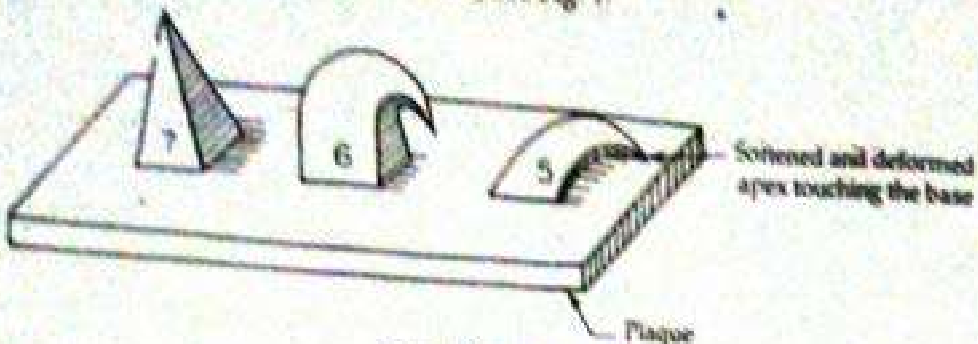


Fig. 1. Seger cone-test.

Table 3. *Seger-cone numbers and fusion temperatures of seger cones at 10°C/minute heating rate*

Seger-cone number	*Temperature (°C)*
1	1110
5	1180
10	1300
15	1435
20	1530
30	1670
35	1770

(b) ***Refractoriness-under-Load (or Strength).*** Temperature resistance and load bearing capacity are the two essential qualities of a refractory. This is due to the fact that commercial refractories which are used for lining high temperature furnace are expected to withstand varying loads of the charge. Hence they should possess high strength and excellent temperature resistance.

Measurement. Seger cone test is not applicable for the measurement of strength. Because, some refractories soften gradually over a range of temperature, but under appreciable load, they collapse, far below their true fusion temperature. High alumina bricks and fire-clays are examples of such refractory materials. There are some other refractory materials like silica bricks which exert good load bearing characteristics upto their fusion temperatures as they soften over a relatively narrow range of temperature. Thus, for good results, Refractoriness Under Load (R.U.L.) test is performed by applying a load of (3.5 or 1.75 kg/cm^2) to the refractory specimen (of size 5 cm^2 and 75 cm high). The sample is then kept in carbon-resistance furnace and heating is started at the rate of 10°C/minute. The height of the specimen is plotted vs. temperature and R.U.L. is expressed as the temperature at which 10% deformation takes place.

Based on R.U.L. test, refractory materials are classified into following three categories :

(i) *A high heat-duty brick,* (which does not deform more than 10 percent at 1350°C).

(ii) *An intermediate heat-duty brick*, (which does not deform more than 10% at 1300°C).

(iii) *A moderate heat-duty brick* (which does not deform more than 10% at 1100°C).

(c) ***Dimensional stability.*** *"Dimensional stability is the resistance of a material to any change in volume when it is exposed to high temperatures, over a prolonged time."*

Types of dimensional changes

(i) *Permanent contraction.* When a refractory is subjected to high temperatures for long duration, either low fusible constituent melts away forming liquid which fills the pores of the refractory body causing shrinkage and vitrification. (Fireclay brick show such type of behaviour) or transformation of one crystalline form of material into another more dense form can also take place. For example, consider magnesite brick :

$$\underset{(\text{sp. gr.} = 3.05)}{\text{Amorphous MgO}} \xrightarrow{\text{High T}} \underset{(\text{sp. gr.} = 3.54)}{\text{Crystalline, Periclase}}$$

With the increase in density, there is shrinkage in magnesite brick.

(ii) *Permanent expansion.* Transformation of one crystalline form of refractory into another of low density leads to expansion when a refractory is subjected to high temperatures for longer duration. Silica brick is one such example, which undergoes permanent expansion in service. For instance, crystalline transformation in silica brick is given below :

$$\underset{(\text{sp. gr.} = 2.65)}{\text{Quartz}} \longrightarrow \underset{(\text{sp. gr.} = 2.26)}{\text{tridymite}} \longrightarrow \underset{(\text{sp. gr.} = 2.32)}{\text{cristobalite}}$$

(d) ***Chemical inertness.*** The refractory material which is used as liner for furnace walls should be chemically inert to the chemicals charged into a furnace. It should not react with the reactants, slags, furnace gases, fuel ashes and the products involved inside the furnace. Such reactions can contaminate the product and/or gradually corrode the furnace. Hence, it is inadvisable to employ an acid refractory in contact with an alkaline product or vice-versa.

(e) ***Thermal expansion and contraction.*** A good refractory material should have least possible coefficient of thermal expansion. Since like other materials, refractory also expands when heated and contract when cooled. Repeated expansion and contraction contribute much towards rapid wear and tear of the refractory structure and its rapid breakdown. Sustained strong binding between the refractory lining and base structure and within the refractory matter is possible only when the thermal effect or volume (coefficient of expansion) is negligible. Due to thermal shock, a substandard refractory develops cracks and then detaches itself from the furnace wall. It is essential therefore, allowance has to be made for thermal expansion.

(*f*) ***Thermal conductivity.*** It is amongst one of the important properties of refractory material since it determines the amount of heat transmission or heat loss due to radiation through it.

Refractories with low thermal conductivities are used for lining the walls of blast furnace, copper hearth furnace etc. because they minimize the heat losses to outside by radiation and help in the maintenance of high temperatures inside the furnace. On the other hand, refractories with high thermal conductivities are used for lining the walls of muffle furnace, coke-oven retorts etc. because in these cases efficient heat transfer from the outer surface to charge is needed.

Hence, depending upon the type of furnace, refractory materials of high or low thermal conductivities are required by industrial operations.

(*g*) ***Resistance to Corrosion and Erosion.*** The higher temperatures at which the furnace is operated, viscosity of slag decreases which accelerate the chemical reaction between the slag and refractory lining. This might lead to corrosion of refractory lining. Greater wetting of the refractory by the slag also increases corrosion. *Erosion* is gradual wearing away of a material from its surface due to the mechanical action of flue gases escaping at high velocities, carbon-particles and descending hard charge inside the furnace. Erosion produces cavities on the surface of refractories which in turn increase the probability of corrosion.

For a refractory to last longer, it is desirable that it should have excellent corrosion and erosion resistance. This property is very important for the selection of refractory material for by-product coke-oven wall and lining of discharge ends of rotary cement kilns etc.

(*h*) ***Electrical conductivity.*** A refractory material of low electrical conductivity is desired for lining the walls of electrical furnace. For proper selection of refractory material it should be always remembered that electrical conductivities of these material increases with rise in temperature. In general, all refractory materials, (except graphite) are poor conductors of electricity.

(*i*) ***Porosity.*** *Porosity* of a refractory material is the ratio of its pore's volume to the bulk volume. Pores are present in all refractory materials and these can be open or closed. Porosity affects many characteristics of a refractory material. For instance, flue gases, slag and/or molten charge can penetrate to greater depth and may react and reduce the life of refractory material of porous refractory. Porosity can also increase the thermal shock resistance. In addition, air is entrapped in the pores and increase the insulation characteristics of porous bricks. In contrast, the densest and least porous bricks have the highest thermal conductivity, strength, resistance to abrasion and corrosion.

(*j*) ***Thermal spalling.*** Rapid changes in temperature, cause uneven expansion and contraction of refractory material, thereby leading to development of internal stresses and strains. This in turn are responsible for cracking, breaking or fracturing of a refractory brick or block under high temperature, collectively known as *thermal spalling*. Thermal spalling can also be caused by the variation in the coefficient of expansion due to slag penetration in the refractory brick. A good refractory must show a good resistance to thermal spalling. Thermal spalling can be decreased by minimising the development of internal stresses by :

(*i*) Using a refractory with high porosity, good thermal conductivity and low coefficient of expansion,

(*ii*) Avoiding sudden temperature changes,

(*iii*) Proper furnace design.

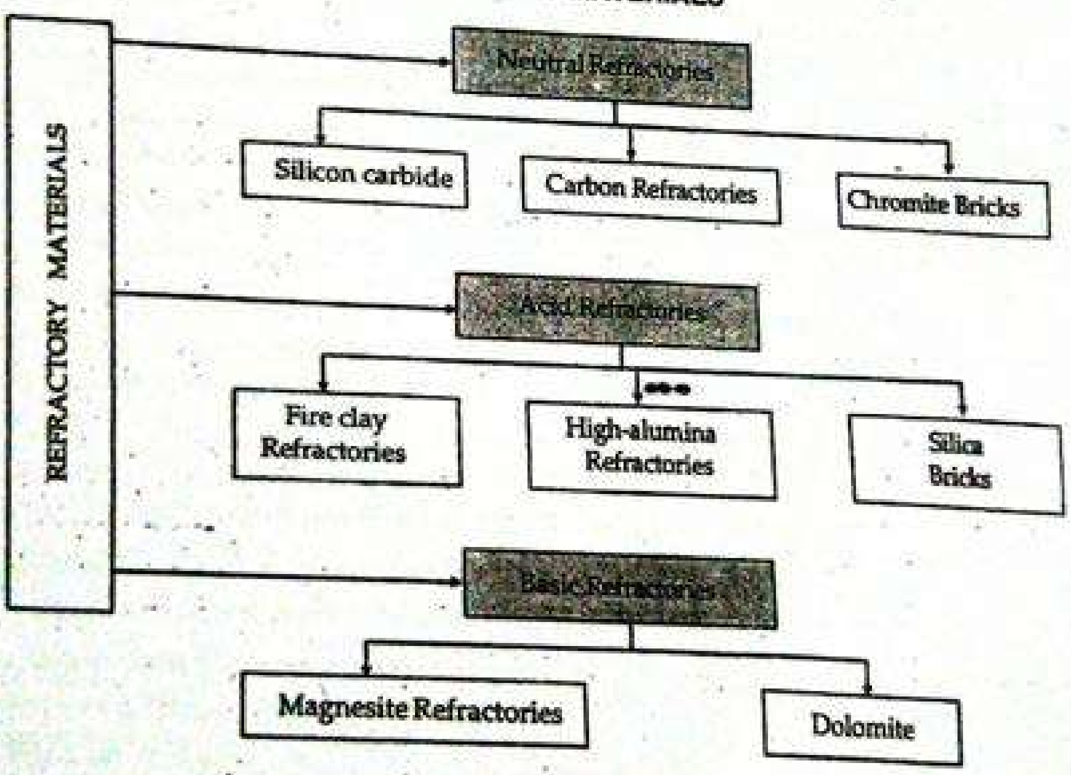
(k) *Permeability.* *"It is a measure of rate of diffusion of molten solids, liquids and gases through the connected pores of refractory."* The higher the porosity of a refractory brick, the more easily it is penetrated by gases and molten fluxes. Permeability depends on the size and number of connected pores. A good refractory material should show low permeability.

(l) *Texture.* Texture can be coarse or fine. Porosity of coarse or light textured bricks are higher than fine or dense-textured bricks. That's why coarse textured refractory bricks have

(i) good resistance to thermal spalling,
(ii) low crushing strength, and
(iii) low abrasion and corrosion resistance.

(m) *Heat capacity.* The dense and heavy fire-clay bricks have higher heat capacity and as such are best suited for regenerators, checker-works as in stoves for blast furnaces, coke ovens, glass furnaces etc. In contrast, intermittently operated furnaces require refractory material of low heat capacity (*i.e.*, light weight refractory brick). Because in them working temperature of the furnace is achieved with lesser consumption of fuel and in lesser time.

4 SOME IMPORTANT HIGH REFRACTORY MATERIALS



Three Important classes of Refractory materials

I. Neutral Refractories

(i) *Silicon carbide (carborundum) Refractories*

Preparation : Carborundum is made by heating a mixture of coke (40%) and sand (60%) together with some saw dust (it helps in increasing the porosity) and salt (it helps in the removal of iron etc., in the form of volatile chlorides) in an electric furnace at 1500 °C. The SiC in the form of interlocked crystals are formed

Applications :

(*a*) Fire clay refractories are mostly consumed by steel industries as these are used for the lining of blast furnaces, open hearths, stoves, ovens, crucible furnaces etc.

(*b*) These are also widely used in foundries ; lime, continuous ceramic, pottery and metallurgical kilns ; glass, brass and copper furnaces ; cupolas etc.

(ii) *High-alumina Refractories*

When the alumina (Al_2O_3) content in the fire clay brick reaches above 47.5% then it is called high-alumina brick.

Preparation : It is made by mixing calcined bauxite (Al_2O_3) with clay bind.

Properties. Because of the high alumina content, these bricks have more refractoriness, better slag resistance, inertness to CO and stability to natural gas environment upto 1000°C.

Applications : High alumina refractories having 75% Al_2O_3 are known as '*high-duty bricks*' and find applications in the hottest zones of cement rotary kilns, combustion zones of oil-fired furnaces, aluminium melting furnaces etc.

High alumina refractories containing 50 to 60% Al_2O_3 are known as '*medium-duty bricks*' and find applications in linings of portland cement rotary kilns, soaking pits, reheating furnaces, hearths and walls, etc., which are subjected to high abrasion.

(iii) *Silica Bricks*

Preparation. The raw materials used for the manufacture of silica bricks are quartz, quartzite, sand, sandstone, ganister etc. Siliceous rock is first crushed and ground with 2% lime & water. The resultant thick paste is then made into bricks by machine pressing. After drying, bricks are burnt in kilns. In about 24 hours, the temperature is slowly raised to about 1500 °C. This high temperature is maintained for about 12 hours. This step is essential since it allows quartzite to be converted into cristobalite (allotropic transformation) careful cooling is then done & it takes about 1 to 2 weeks. Cristobalite is slowly changed into tridymite during cooling and in the final brick, the mixture of two results.

Properties :

(*a*) Silica bricks are yellowish in colour with brown specks throughout the body.

(*b*) These bricks are acidic & are therefore suitable for acidic furnace charges.

(*c*) Silica bricks are remarkable for their load bearing capacity. They can withstand a load of about 3.5 kg/cm^2 upto about 1600°C.

(*d*) Silica bricks are not susceptible to thermal spalling at temperature below 800°C

(*e*) These bricks are light & possess high rigidity & mechanical strength.

(*f*) These bricks do not contract in use.

Applications :

Silica bricks are used in lining roof arches of open hearth furnaces & reverberatory furnaces, gas retort and walls of coke ovens.

III. Basic Refractories

(i) Magnesite Refractories

Preparation : It is made from dead-burnt magnesite grain which are property crushed into powder form of proper size. Molasses or sulphite lye is used as a binder. Thermal shock resistance is imparted to the magnesite refractory by adding 2 to 6% of alumina. The ingredients are blended after adding requisite quantity of water and the mix is aged for 1 to 10 days to ensure complete hydration of any free lime present. The mix is then moulded into bricks and temperature is slowly increased to 1500°C. The bricks are kept at this temperature for about 8 hrs. and then slowly cooled.

Properties :

(*a*) Magnesite refractories have high resistance to basic slag and low resistance to acid slag.

(*b*) They possess good crushing strength.

(*c*) It can be used up to 2000°C without load and under a load of 3.5 kg/cm^2, it can be used upto 1500°C.

(*d*) It has poor resistance to abrasion and spalling.

Applications :

(*a*) Mainly used in steel industry for the lining of basic converters and open-hearth furnaces.

(*b*) These refractories are also used in the roofs of non-ferrous reverberating furnaces *e.g.*, those used for Pb, Cu and Sn.

(*c*) Also used for the lining of refining furnaces for gold, silver and platinum etc.

(ii) Dolomite Refractories

Preparation : After washing and crushing, Dolomite (mixed carbonate of calcium and magnesium, ($CaCO_3 . MgCO_3$) is calcined. Dolomite decomposes to give CaO and MgO during calcination. This is then mixed with silicate (which acts as binder) and water. The mixture is allowed to stand for sometime and then moulded into bricks. The bricks are then fired at 1500 °C for about 24 hrs. in a kiln.

Properties. Compared to magnesite bricks, dolomite bricks posses

(*a*) less strength and low resistance to thermal shock,

(*b*) more softness and porosity and hygroscopicity and greater shrinkage. Stabilized dolomite bricks do not have the above mentioned limitations and it is made by incorporating serpentine ($MgO.SiO_2$) in dolomite before calcination in the initial stages. Stabilized dolomite bricks have very good resistance to basic slags.

Applications :

(*a*) Dolomite refractory is generally used as a repair material.

(*b*) Stabilized dolomite refractory is used for basic electric furnace linings, ladle-linings, open-hearth furnaces etc.

(*c*) Stabilized dolomite refractory material is also used as cheap substitute for magnesite bricks.