

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.

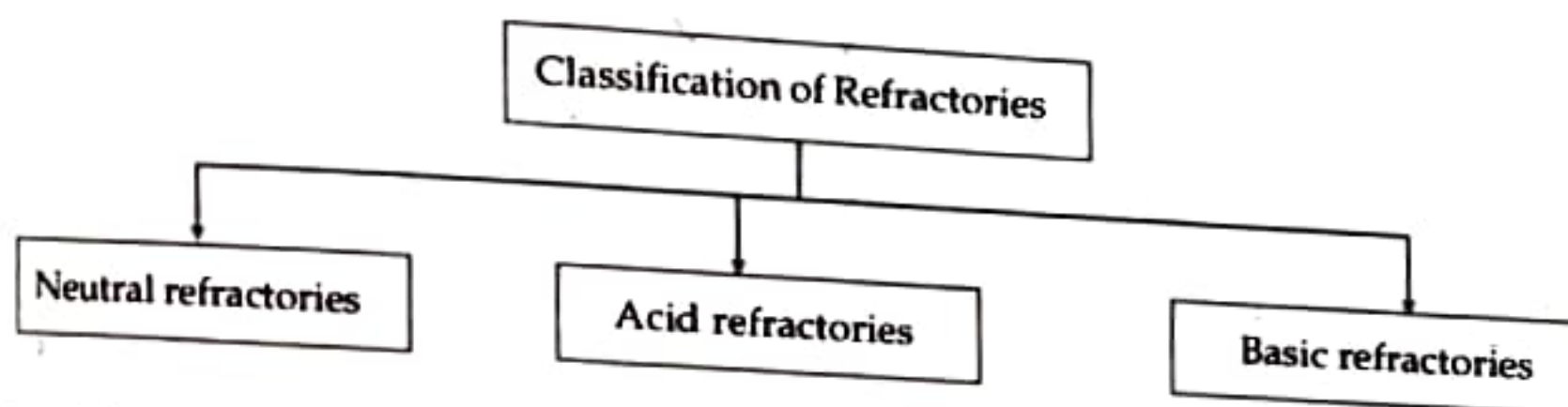
The existence of many ceramic materials with quite different properties is due to the fact that many combinations of the metallic and non-metallic atoms, with general structural arrangements for each combination, are possible. The constituents of ceramic material may form covalent or ionic bonds. Most 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.

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 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 ($FeO \cdot CrO_2$)

(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.

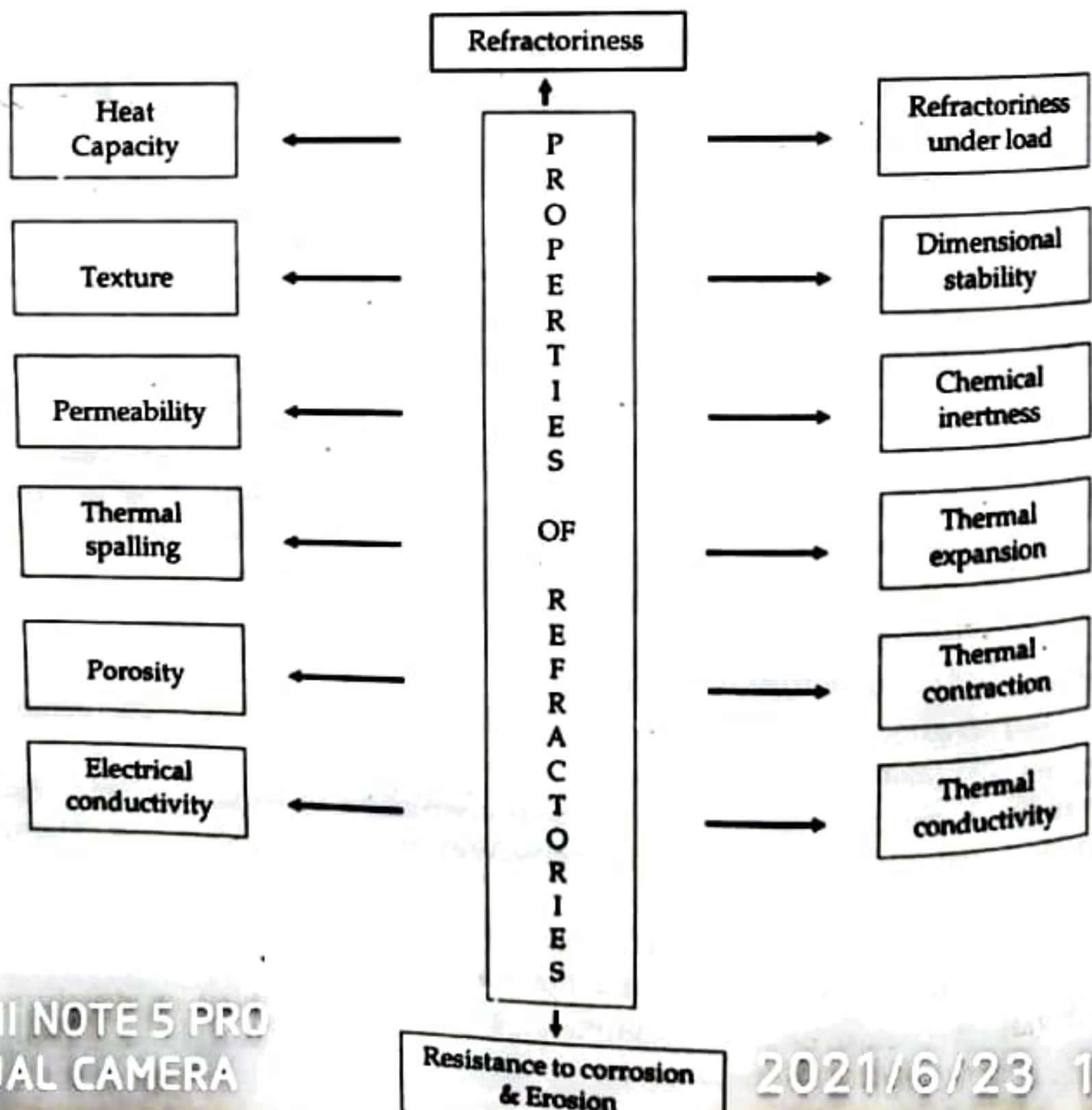
- (v) They should be chemically inert towards corrosive action of molten metal, gases and slags, produced in its immediate contact in furnaces.
- (vi) They should not crack at the operating temperatures.

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:



(iv) **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.

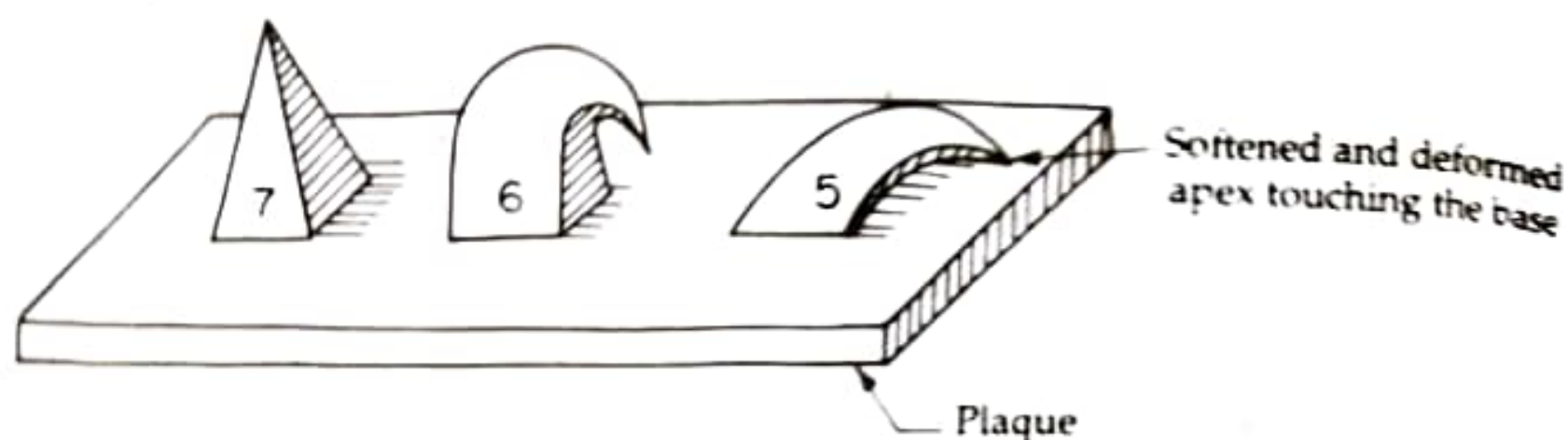


Fig. 1. Seger cone-test.

Table 3 : Seger-cone numbers and fusion temperatures of seger cones at $10^{\circ}\text{C}/\text{minute}$ heating rate

Seger-cone number	Temperature ($^{\circ}\text{C}$)
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 $(3.5 \text{ or } 1.75 \text{ kg}/\text{cm}^2)$ 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 $10^{\circ}\text{C}/\text{minute}$. 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:

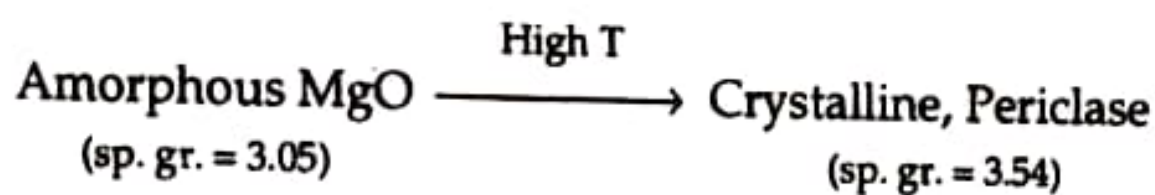
- A high heat-duty brick, (which does not deform at 1350°C).

- (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."

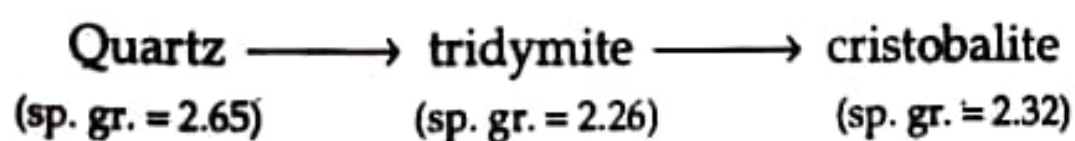
Types of dimensional changes

(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 :



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 :



(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.

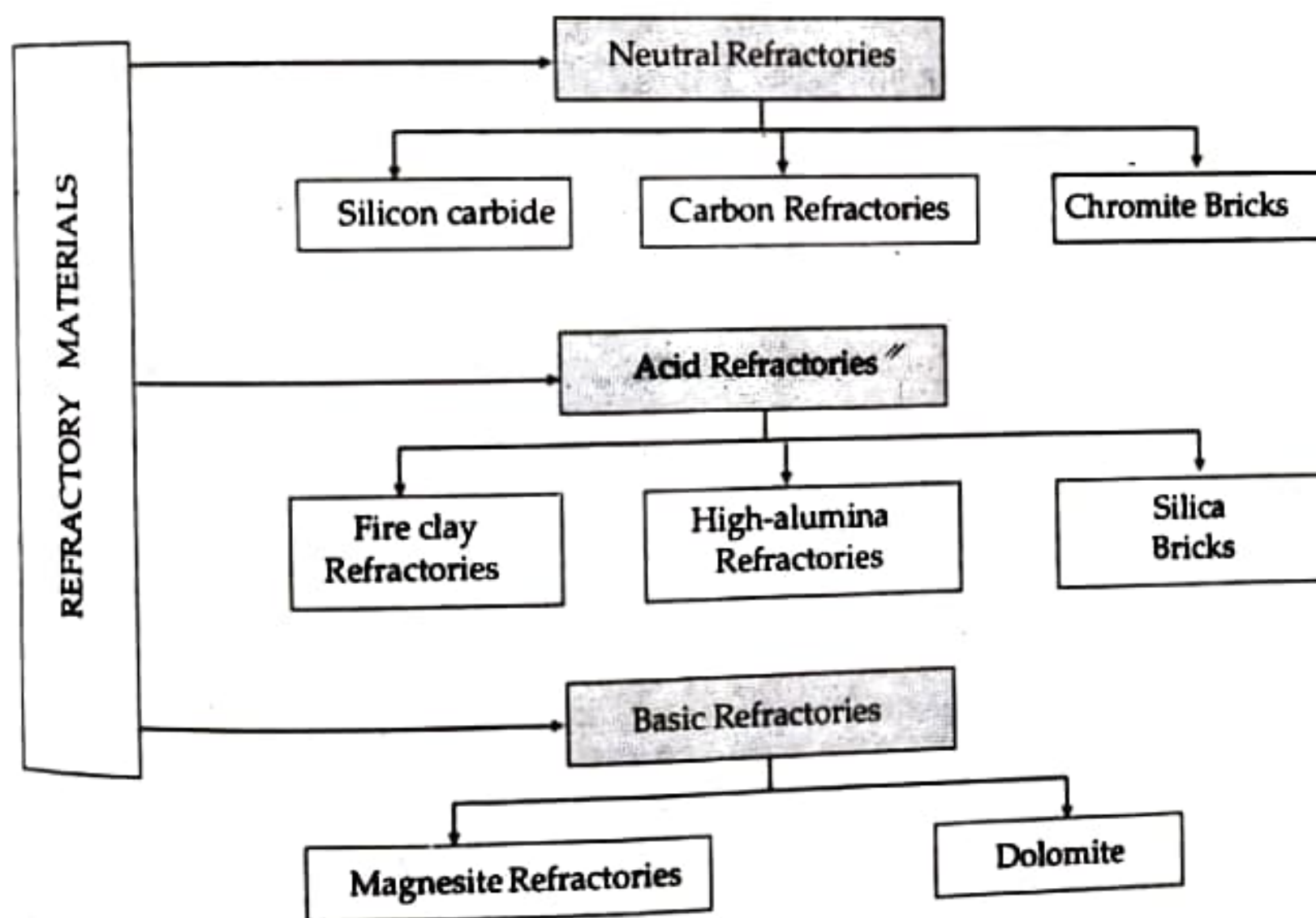
(k) **Permeability.** "It is a measure of rate of diffusion of molten solids, liquids and gases through the connected pores of refractory." The higher the porosity of a refractory brick, the more easily it is penetrated by gases and molten fluxes. Permeability depends on the size and number of connected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

1. 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

this method. These interlocked crystals are crushed ; sized and suitably graded for getting dense packing. These are then mixed with bonding agents ($\leq 10\%$) like plastic, fire clay, graphite or silicon nitride for imparting superior oxidation resistance. After mixing with bonding agent, final firing is done in reducing atmosphere at about 1500°C . It is interesting to note here that if SiC particles are mixed with glue (temporary binding agent) and fired at 2000°C , self-bonding type of SiC refractory bricks (having intercrystalline bonds) results.

Properties : (a) SiC refractories have high thermal conductivity, low thermal coefficient of expansion and thus have ability to withstand sudden temperature fluctuations.

(b) The SiC bricks are extremely refractory and possess high mechanical strength. They can withstand loads in furnaces even at higher temperatures ($\geq 1650^{\circ}\text{C}$). They possess excellent resistance to spalling and abrasion.

(c) Chemical resistance of SiC refractories are also good. They have high resistance to reducing atmosphere and acid slag, medium resistance to oxidising atmosphere and low resistance to basic slag.

In oxidising atmosphere, at temperature of about 950°C , SiC bricks have a tendency to oxidize to Si. This tendency can be minimized by thin layer of zirconium coating.

Applications :

- (a) SiC refractories (lime bonded), are mainly used in muffles, because of their good thermal conductivity,
- (b) It is also an ideal choice for recuperaters because of good resistance to spalling under repeated temperature fluctuations and ability to absorb and release heat rapidly,
- (c) Partition walls of chamber kilns, coke ovens and furnace floors are also made by SiC bricks,
- (d) Globars (furnace's heating elements in the form of rods and bars) are also made by SiC refractory because of its high electrical conductivity.
- (e) High conductivity crucibles are made from SiC bonded with tar.

(ii) Carbon Refractories

Preparation : They are made by ...
or graphite ...

Applications :

- (a) Carbon and graphite bricks are mostly used as construction materials for electrodes.
- (b) They are also used for linings of chemical resistant equipments, atomic reactors, electric furnaces, heat-transfer systems, and in aluminium, copper and lead smelting furnaces.
- (c) Crucibles made from graphite are also widely used in industry. The crucible surface is coated with boric acid, borax, soda ash, sodium silicate, CaCl_2 or MgCl_2 in order to prevent oxidation.

Note : Clay or carbon bonded graphite crucibles upto 100 kg capacity are produced by small scale sector in India.

(iii) Chromite Bricks

Preparation : Chromite ($\text{Cr}_2\text{O}_3 \cdot \text{FeO}$) is blended with clay and then firing is done at a temperature of 1500 to 1700°C for the manufacture of chromite bricks.

Properties :

- (a) Chromite bricks are neutral refractories having good slag resistance.
- (b) Their spalling resistance is moderate.
- (c) They possess moderate thermal conductivity & high density.
- (d) Their use temperature is limited to 1800°C.
- (e) They have good crushing strength and refractoriness under load.

Applications : Chromite bricks are used in :

- (a) Furnace linings,
- (b) Sodium carbonate recovery furnaces &
- (c) bottoms of soaking pits.

II. Acid Refractories**(i) Fire clay refractories**

Preparation : Fire clay refractories are made from raw and calcined aluminosilicate which are known as fire clays because they can withstand high temperatures. Calcined fire clay, known as the "Grog", accounts for 50% or more of the batch mix. The exact properties of the constituents depend on the type of bricks to be made. For example, feebly acidic fireclay bricks contain 55% SiO_2 and 35% Al_2O_3 while nearly neutral fire clay bricks contain 40% SiO_2 and 55% Al_2O_3 . The balance in both of them consists of K_2O , FeO , CaO , MgO etc. (Accessory oxides in the clay).

Properties :

- (a) Depending on the content of iron oxides, fireclay bricks are light yellow to reddish-brown in colour.
- (b) Depending on the SiO_2 content, the fireclay bricks show acidic character.
- (c) Depending on the SiO_2 content, the fireclay bricks show resistance

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, and in the heart and walls of coke ovens.