# CERAMIC

# REFRACTORRY

# TECHNOLOGY -1

## UNIT-1 Definition and classification of refractories

## 1.0 INTRODUCTION TO CERAMIC REFRACTORY

Most of the industries required high temperature operation which depend on the refractories materials or bricks made by refractories industries. Among these iron and steel industry is the greatest consumer of refractories. It takes away about 70-75% of the total productions of refractories.

India has excellent and huge deposits or raw materials for refractories. In the industrialization of a country refractory plays an important role. Steel forms its back bone. All metallurgical industries, glass, enamel, pottery, white ware, cement, power generation etc. ultimately depend upon the supply of refractories.

Refractories are the materials which protect industrial equipments (generally kiln or furnaces) and vessels. From industrial point of view, refractory materials are those which do not soften by fusion at working temperature. The important features of refractories, therefore are excellent resistance to heat and thermal shock, chemical attack (Corrosive action of slag or molten mass, fluxes or furnaces atmosphere), resistance to abrasion by the charge or the flue gases, moving solid particles or molten mass, dust laden gases at high temperature. They should also bear the load at ordinary temperature and must not deform under load at high temperature. Every industrial concern is mainly deviation its energy at the best production at the cheapest cost and hence the cost of refractory become a vital questions. If proper refractory are not chosen, not only the cost increases but the rate of production is also impacted.

## 1.1 DEFINITION OF “REFRACTORY”-

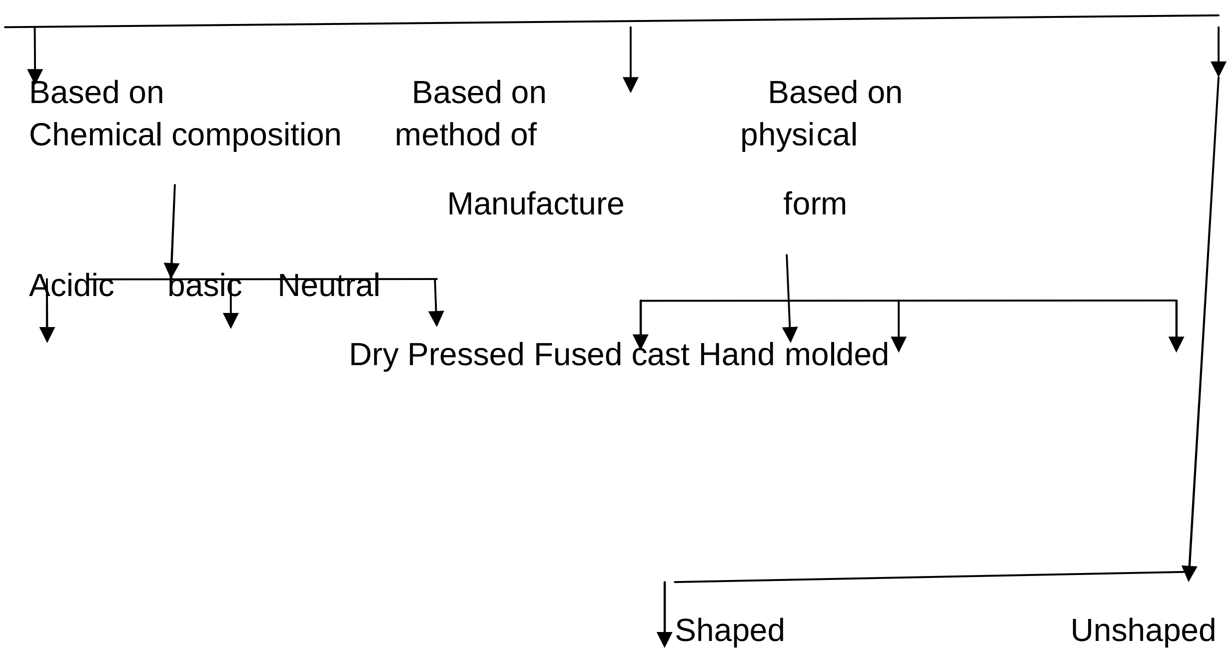
Refractories are the materials which are “hard to fuse”. “The refractories are class of materials which can withstand at high temperature without fusing or deformation in shape and size, resist the action of corrosive liquids and dust laden currents of the hot gasses”.

In technology terms refractories referred to the materials used to make furnaces kilns, stoves, driers, and critical parts of air credit, jet engines and aerospace craft operating at high temperature.

## 1.2 CLASSIFICTION OF REFRACTORIES

Refractories are classified on the basic of chemical composition, method of manufacture and physical from as shown below-

CLASSIFICATION OF REFRACTORIES




## 1.3 CLASSIFICATION BASED ON CHEMICAL COMPOSSITION

Refractories can be classified on the basis of their chemical behavior i.e., their reaction to the type of slag’s. Accordingly refractory materials are of three classes, namely Acidic, Basic and Neutral.

I **Acidic refractory**- Acidic refractories are those refractories which are not attacked by acidic slag's (alkaline), but attacked by basic slag's (alkalis). These are used in places where slag and atmosphere are acidic.

example - Fireclay (Low heat duty, intermediate heat duty, super duty) Silica, Semi silica, Kyanite, Sillimanite, high alumina refractory etc.

**II** **Basic Refractories**- Basic refractories are those which are not attacked by basic slag's, dusts and fumes at elevated (high) temperature but attacked by acidic slag's.

These have high coefficient of thermal expansion but not much resistant to thermal shock, hence they are not used generally for intermittent (batch) kilns. These are used in furnace where environment is basic. example- non ferrous metallurgical operation, Magnesite, Dolomite, Magnesite – chrome. Chrome- Magnesite refractory etc.

III **Neutral Refractories**- These refractories are neither attacked by acidic slag's nor by basic slag's.

These are stable to both acids and based and are used in areas where slag and atmosphere are either acidic or basic.

## THESE REFRACTORIES INCLUDES-

a. Various forms of carbon (graphite, charcoal and coke), Chromites.

b. Artificial or synthetic refractories like- zirconium carbide and silicon carbide.

c. Metals used as refractory like iron, copper, molybdenum, nickel, platinum, osmium, tantalum, thorium, tungsten, vanadium and zirconium.

## CLASSIFICATION BASED ON METHOD OF MANUFACTURE

Another way of classifying refractories is by the manner in which they are shaped. The refractories can be manufactured by either of the following methods.

**a Dry pressed refractories-** these are those which are pressed with the help of hydraulic or mechanical press in dry state.

1. **Hand molded refractories-** these are molded in wooden moulds in plastic condition.

2. **Fused cast refractories-** these are those which are first melted and then casted in desired shapes.

**CLASSIFICATION BASED ON PHYSICAL FORM**

Refractories can also be classified according to physical form. These are Shaped and Unshaped refractories. The former is commonly known as refractory bricks and the later as “monolithic” refractories.

1. **Shaped refractories** - Shaped refractories are those which have fixed shape. These are also called wall bricks. Bricks shapes can be standard shapes can be standard shapes and special shapes. Standard shapes have dimension that are conformed to by most refractory manufactures and are generally applicable to kinds and furnaces of same type. Whereas special shapes are specifically made for particular kiln and furnaces. This may not be applicable to another furnace or kilns of same type.

2. **Unshaped refractories -** Unshaped refractories are without define form and are only given shape. Upon application. These are categorized as Plastic refractories, ramming mixes, castable, gunning mixes, fettling mixes and mortars.

**Insulating refractories-** A refractory suitable for minimizing heel losses and thus achieving heat conservation in the furnace is called insulating refractors.

They have high porosity, low thermal conductivity and high thermal insulation proprieties. These are produced from asbestos, fire clay, kieseiguhr etc. At low temperature slag wool, glass wool and vermiculite are also used as insulating materials. For high temperature thermal insulation applications foam ceramics and ceramic fiber and wool are used.

**Cermet refractories –** These refractories are a combination of ceramic materials (e.g.- oxide, nitride borides etc) and metallic or metallic alloys materials. It has the combination of goods properties of both metallic and ceramic materials e.g.- high strength and resistance to high temperature cermets are used in nuclear reactors, missiles and space crafts etc.

**Special refractories-** these are very expensive refractory materials used for making crucibles and furnaces for special experimental purpose where cost of refractory is no consideration. They are not very common due to their manufacturing limitation.

Special refractories include pure oxide (eg – magnesia silica, alumina, Beryillia, thoria etc.

Other special refractories are Sialons, zircon, carborundum, alundum (a mixture of fused alumina and clay), sillimanite, electro cast blocks of mullite, magnesia and mixtures of chromite, bauxite and magnesia.

## PROPERTIES OF REFRACTORY -

1. Refractories:- It is the ability of a refractory to withstand high temperature without getting deformed or fused.

2. R.U.L:- It is the property of refractory by virtue of which it resists the combined effect of heat and load laying on it.

3. C.C.S:- Cold crushing strength of a refractory determines that how much load a refractory can withstand in cold condition without breaking or deformed.

4. Density:- It is defined as mass per unit volume of refractory.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

5. Porosity:- Porosity is a measure of open pores in a material to the total volume of material.

$$\text{Porosity} = \frac{\text{Volume of pen pores}}{\text{total volume of open and closed pores}}$$

6. Spalling resistance or T.S.R:- It is the ability of refractories to retain its original shape and size without cracking, spelling or flaking; when subjected to sudden change in temperature/ heat.

7. Slag resistance :- It is the property of a refractory by which it resists the attack of slag (acidic or basic) on it without any deformation (corrosion or Erosion).

8. Erosion resistance :- It is the property of a refractory which shows that how much resistance it offers to the chipping off the particles from it. Erosion takes place when molten metal or gas carry dust and slag particles. When those slag and dust particles strike against refractory lining, it results in chipping off particles from it.

9. Abrasion resistance:- It is the property of refractory which shows that how much resistance it offers when refractory lining come in contact with moving charge; which rubs against it and subject it to wear.

10. Modulus of rupture :- It is the flexural breaking strength of a refractory. It is measured at room temperature and expressed in kilogram per/square centimeter of kg/cm2.

## METHODS OF MANUFACTURING OF REFRACTORY-

1. Grinding- firstly raw materials are ground, so their proper sizes of material are obtained Ratio of course to fine particles should be even. This ratio is normally maintained at 55:45 equipments used for this purpose are various types of crushers, pulverizer, hammer mills, bill mills, shaking tables and screen etc.
2. Pre-treatment- the main pre-treatment given to refractory raw materials is its firing/calcinations at high temperature for considerable periods of time which bring about the complete mineral conversion and hence stabilizers the material. The constituents of the finished refractories produced by reaction between the solid particles of raw materials are rarely completely in equilibrium because it is seldom feasible to actually melt and cast these refractory materials. Natural silica mainly containing quartz which is not stable at high temperature, but undergoes transformation to its allotropic forms tridymite and βcristoballite involving high volume changes.

   Thus raw silica expands considerably when heated to high temperatures and destabilization of silica become necessary.

3. Chemical composition- the chemical composition of the refractory should be such that the surrounding do not chemically attack the refractory and corrode it. Acidic refractory should not be used in a furnace heating a basic material. Otherwise the brick will react with the furnace stock and corrode, hence it will reduced.
4. Mixing- Ground refractory material is mixed with the binding material in such a way that plastic materials are equally distributed throughout the mass to facilities easy moulding. Mixing is usually carried out in pug mills for even distribution of fine and coarse particular in the whole mass. Recalculated amount of water, additives, binding materials and mineralizes are added and the mass is mixed thoroughly to ensure a product of uniform composition and uniform distribution of fine and coarse grains plastic and bond materials.

For easy moulding and development of useful properties in the fired refractories. To ensure increased plasticity for easy moulding, mixture is allowed to remain as such for a day or more.

Mixing can be dry, semi-plastic or wet type 14-20% water is used in wet mixing which are mostly used for hand moulding. Semi plastic mixtures have lower percentages of water to achieve semi-state of plasticity where as the dry mixture include non-plastic basic mixes and clay mixes containing <5% water, since mixing with so little water is difficult, water as a fine spray or mist is used to achieve proper mixing due to requirement of high moulding pressures, semi-plastic and dry mixture are machine pressed. Clay mixtures are also obtained in the form of colloidal solution suitable for moulding by slip casting.

5. Moulding- It is done mechanically by applying high pressure or by hand to increase density and strength of the refractory.

Moulding which follows mixing of refractory materials is done either by hand or machine (by pressing or extrusion). Hand moulding is carried out in wooden boxes and is cheaper than machine on a jobbing basic. However, machine moulding has more practical applications and is cheaper for mass production of standard refractory shapes. Machine moulded refractories have higher strength and density than hand moulded refractories.

Machine moulding can be used for semi-plastic mixture using moderate moulding pressure.

Extrusion is usually used to get the rough shapes of approximate dimensions which are subsequently pressed to exact shapes. Machine moulding of dry mixture requires a pressure of about 1000 kgf/cm2 or more.

Density and strength of the refractories increases on de-airing due to decrease in lamination and cracks. Density increase is due to elimination of air of a lower density than the refractory material and or closing of voids.

The method used for moulding refractories of hollow and other special shapes is slip casting in which a colloidal suspension is poured into a plaster of Paris moulds which absorbs the water and causes deposition of uniform layer of clay on the walls of the mould on deposition of desired thickness of clay, the extra mixture in suspension is poured out of the mould resulting in hollow refractories with irregular interval counters.

Powder pressing is used for moulding refractories involving dry compacting or slightly damp refractory powder mixture in metallic dies using sufficient high pressure to produce strong and dense refractory shapes.

6. Drying- it is done at slow rate to avoids voids and high shrinkage. During of moulded refractory increase its green strength by removing moisture and thus making them safe for subsequent handling. Drying is usually carried out under shade on large drying floors. Floors heated by waste heat from kilns are also used where refractories are laid out in open arrays.

For faster drying of refractories of constant shape and sizes, tunnel kiln are used, where raw refractories are stacked in bogies or placed on belts moving through a tunnel against a stream of hot air.

For during heavy refractories of indicated shapes, controlled humidity dries are specially used Draying rate of fire bricks should be very low to avoid cracks formations as they are liable to maximum shrinkage on drying.

7. Firing/burning- Bricks are burnt in kiln (down draught kiln or tunnel kiln) to remove water of hydration, vitrification and development of stable mineral forms. Shrinkage in volume up to 30% occurs during burning. Burning or firing of refractories which follows their drying facilities developments of stable mineral forms in them and high crushing strength of finished products.

Degree of firing of silica bricks is indicated by its specific gravity. High specific gravity of 2.5 indicates the presence of considerable amount of unconverted quartz in the refractory where as a specific gravity 2.32 to 2.37 indicates adequate firing and transformation of quartz to cristoballite and tridymite.

Bricks firing is done either in down draught, batch type or tunnel kilns. These kiln firing is time consuming due to involvement of three stage operation namely brick charging, firing and cooling.

**FIRING TEMPERATURE OF SOME TYPICAL COMMON BRICKS AS FOLLOWS :-**

| SNO. | REFRACTURY TYPE | FIRING TEMPERATURE C |
|---|---|---|
| 1 | Fire clay bricks | 1250-1400 |
| 2 | High alumina bricks | 1450-1550 |
| 3 | Silica bricks | 1450-1510 |
| 4 | Chrome bricks | 1450-1650 |
| 5 | Magnesite bricks | 1450-1650 |
| 6 | Direct bonded basic brick | 1650-1760 |
| 7 | Silicon carbide bricks | 1370-1510 |

## COMPOSITION OF VARIOUS REFRACTOURY BRICKS:-

| SNO | Principal Constituents% | SiO2 | AI2O3 | Fe2O3 | Cr2O3 | MgO | CaO |
|---|---|---|---|---|---|---|---|
| 1. | Fire bricks | 50-70% | 25-38% | 2-5% | - | 0.5-1% | 05-1% |
| 2. | Aluminous Fire bricks | 50-55% | 38-45% | 2-4% | - | 0.5-1% | 0.5-1% |
| 3. | Semi silica bricks | 75-90% | 8-15% | 1-2% | - | 0.5-1% | 0.5-1% |
| 4. | Silica bricks | 94-95% | 0.5-2% | 0.5-1.5% | - | 0.5-1% | 2-2.25% |
| 5. | Sillimanite bricks | 25-35% | 55-65% | 0.5-1.5% | - | 0.5-1% | 0.5-1% |
| 6. | Megnesite bricks | 1.5-5% | 1-4% | 2-8% | - | 84-92% | 2-5% |
| 7. | Chrome bricks | 3-10% | 10-25% | 12-25% | 35-45% | 15-35% | 2% |
| 8. | Chromo-Magnesite bricks | 3-10% | 5-15% | 8-20% | 20-35% | 40-60% | 1-4% |
| 9. | Dolomite bricks | 12-15% | 2-3% | 2-4% | - | 38-42% | 38-42% |
| 10. | Periclase | 3.0% | 1.0% | 3.0% | 0.5% | 98.0% | 2.5% |
| 11. | Forsterite bricks | 33.5% | 1.0% | 0.1% | 0.5% | 54.5% | 1.0% |

**Selection of refractories-** The selection of the refractories for any particular application is made with a view to achieving the best performance of the equipment, furnace, kiln or boiler and depends on certain properties of the refractories. Further, the choice of a refractory materials for a given application will be determined by the type of furnace or heating unit and the prevailing conditions. e.g.- the presence of slag's, the type of metal charge etc. Therefore, temperature is not only the criterion for selection of refractories.

Any furnace designer or industry should have a clear idea about the service condition which the refractory is required to face. The furnace manufactures or users have to consider the following points, before selecting a refractory.

1. Area of application.
2. Working temperature.
3. Extent of abrasion and impact.
4. Structural load of the furnace.

5. Stress due to temperature gradient in the structure and temperature fluctuations.
6. Chemical comparability to the furnace environment.
7. Heat transfer and fuel conservation.
8. Cost consideration.

**OCCURRENCES OF RAW MATERIAL FOR MANUFACTURING OF REFRACTORIES-**

1. The raw material for fire bricks is fire clay. It occurs in the coal fields of Jharkhand, west-Bengal, Madhya Pradesh, Orissa, Andhra Pradesh.
2. Sillimanite occurs in khasi hills in Assam, near Pipra village in Madhya Pradesh, near the village Pohra in the Bhandara district of Maharashtra, as beach sand in Traven core in Kerala state.
3. Kyanite occurs in Chhota Nagpur in Jharkhand.
4. Silica exist in the form of quartzite deposits in Bihar Sharif and Monghyr district of Bihar, Lotapahar and Brajmada in Orissa.
5. Magnesite occurs in Chalk Hills in Salem district and Dodkanya in Mysore state, ldar in Gujarat, Doongarpur in Rajasthan, Almora district of U.P.
6. Chromite occurs in Mysore, Hassan Kadar, Chitradurg and shimoga in Karnataka, Salem district of tamilnadu, singhbhum of Jharkhand, ratangiri in Maharashtra and ladakh in J & K.
7. Zirconia is available in the form of zirconium minerals, which occurred as beach sand in Kerala.
8. Carbon and Graphite are found in Orissa, Bihar and Karnataka.

**MANUFACTURING UNITS OFREFRACTORIES IN INDIA**

The various manufacturing units in India are as follows

1. Tata Refractories Limited, Belapur, Orissa.
2. Bharat Refractories Limited, Marar, Ramgarh, Jharkhand.
3. Valley Refractories Limited, Chirkunda, Dhanbad, Jharkhand.
4. Miathan ceramics Limited, Chirkunda, Dhanbad, Jharkhand.
5. Hind gulf Refractories, Gandhinager, Kutch, Gujarat.
6. Prajapati Refractories, Thangadh.
7. Carborundum Universal Limited, Ranipet, Tamilnadu.
8. Monolithic refractories, Isanpur, Ahamdabad.
9. Vision refractories Private Limited, Mumbai.
10. Thermo Technologies Private Limited, Delhi.
11. Alwar Refractories Private Limited, Alwar, Rajasthan.
12. OCL India limited, New Delhi.
13. PINC Group, Kilpauk, Chennai, Tamil Nadu.

14. Grind well Norton limited, devanhalli Road, Bangalore, Karnataka.
15. Reliable Refractories Private Limited, Bhilwara, Rajasthan.

These are names of major industries. Most of the industries are located near the places of occurrences of their major raw materials.

## 2.1 Testing of various properties of refractories.

In unit number three you have studied various properties of refractories. To assess these properties you need to test these refractories. Inspection and testing of refractories is important to ensure suitability of a refractory product for an end use. Not only this, testing also help refractory engineer to control process of manufacturing. You most note that results of tests are not of much importance. Their interpretation is important. This is so because no definite correlation between results and their performance is found. This in turn guarantee minimum quality variations and ensure conformity of the product to specific consumer specification. Following are methods used for testing various properties of refractories:-

2.5.1 Pyrometric cone equivalent(PCE)

2.5.2 Refractoriness under load(RUL)

2.5.3 Spalling resistance

2.5.4 Resistance to chemical attack

2.5.5 Permeability

2.5.6 Apparent porosity

2.5.7 True specific gravity and true density

2.5.8 Bulk density

2.5.9 Cold crushing strength(CCS)

2.5.10 Modulus of rupture(MOR)

2.5.11 Permanent linear change(PLC)

## 2.5.1 Pyrometric cone equivalent (PCE)

This test is conducted to determine the softening temperature of refractories to help in selection of refractories to suit specific working temperatures. In this test softening characteristics of cones are compared with standard pyrometric cone in a furnace having neutral or oxidizing atmosphere.



Procedure for testing of refractoriness is as follows:

i. Take one kg of refractory to be tested.
ii. Crush in roll or jaw crushers to a size 5mm.
iii. Ground in a porcelain or agate and passed through 20 micron I.S. sieve.
iv. Pass ground material through magnetic separator to remove iron particles.
v. Mix the material thoroughly with required amount of water and alkali free dextrin or glue.
vi. Make the cones with the help of mould of the shape of a tetrahedron with 8mm sides on the base and 25mm height.
vii. Sintered the cones at 1000 deg Celsius for easy handling.
viii. Arrange the test cones and the standard Pyrometric cones of known softening temperature on plaque with the help of some bonding material as shown in figure 5.1. This material should not react with the cones and reduce their fusibility. Standard cones are chosen keeping in view the anticipated fusion temperature of the test cones
ix. Fix each cone on the plaque forming an angle of 82 degree with the horizontal.

x. Keep the plaque in a suitable furnace either gas fired or electrically heated as shown in figure 5.2.The flame should not directly strike the cones and furnace atmosphere should be oxidizing or neutral.

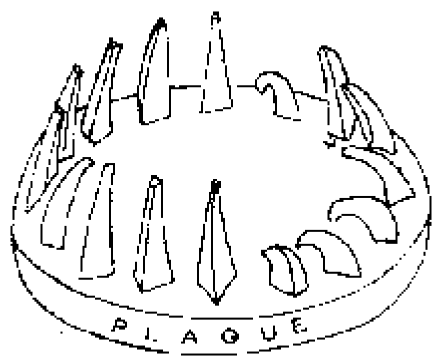



**Figure 5.1 : Arrangement of cones on a plaque**

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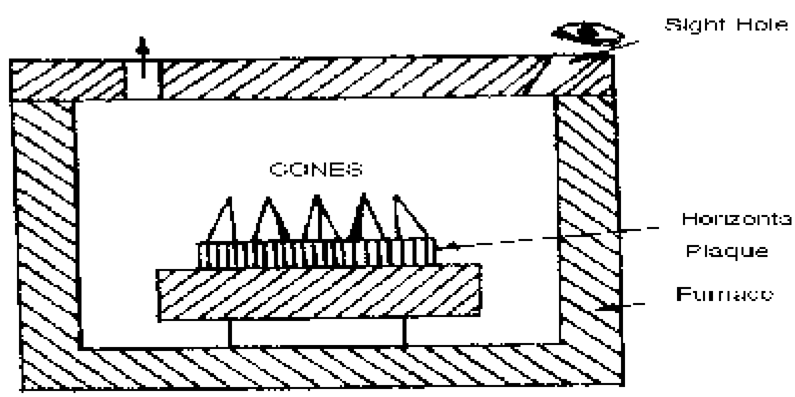


**Figure 5.2 : Fusion Point Furnace**

(xi) Maintain rate heating should as per schedule given in table number 5.2

**Table 5.2 : Heating Schedule**

| Room Temp. to ASTM Cone No. | Time interval (Min.) | Cumulative time (Min.) | End Point ($^{0}C$) |
|---|---|---|---|
| 20 | 45 | 45 | 1621 |
| 23 | 16 | 61 | 1640 |
| 26 | 7 | 68 | 1646 |
| 27 | 7 | 75 | 1659 |
| 29 | 8 | 83 | 1665 |
| 31 | 10 | 93 | 1683 |
| 31.5 | 6 | 99 | 1717 |
| 32 | 7 | 106 | 1724 |
| 32.5 | 3 | 109 | 1743 |
| 33 | 7 | 116 | 1763 |
| 34 | 9 | 125 | 1785 |
| 35 | 9 | 134 | 1804 |
| 36 | 7 | 147 | 1820 |
| 37 | 7 | 148 | 1835 |

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(xii) Observe the softening of cones through a peep hole. It is indicated by top bending over of the cone and tip of the cone touching the plaque surface as shown in figure 5.3

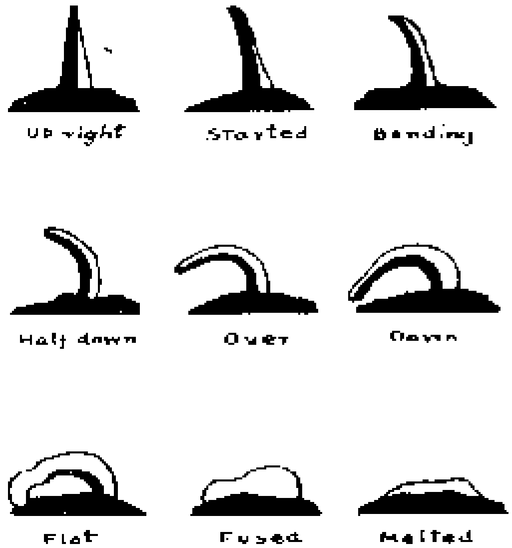


**Figure 5.3 Progressive bending of cones in fusion point furnace (P.C.E.) furnace**

(xiii) Record the softening point of the standard Pyrometric cone which most nearly corresponds in time of softening with the test cone as the P.C.E. of the test cone .If the test cone softens in between two standard cones than the P.C.E. of the test cone is taken as the mean of the two cones.

Sometime instead of bonding the cones with the plaque self supporting cones can also be used as shown in figure 5.4

**Figure 5.4 Self Supporting Cones prior to firing (top) and after (bottom)**

### 2.5.2 Refractoriness under load (RUL)

RUL is a measure of a resistance of a refractory product to deformation when it is subjected to combined effect of load, rising temperature and time.It is the softening temperature of a refractory under loaded conditions corresponding to breaking of refractory brick. Following procedure is used for testing RUL

i. Take a specimen of refractory whose RUL is to be deternmined.

ii. Obtain a cylindrical shape having diameter 50 ± 0.5 mm and height 50 ± 0.5mm by cutting, boring and grinding the central portion of refractory being tested. One of the face of specimen should be original faces of the refractory sample takenforming one of the faces of the finished test specimen.

iii. Check that the refractory specimen must be free from cracks and other macro defects.

iv. Heat the sample in an electric furnace consisting of a refractory tube of 100 to 120 mm internal internal diameter,120 to 150 mm outer diameter and about 500 mm length. This tube can be of corundum, magnesite or mullite as shown in figure 5.5

v. Ensure to keep central 100 to 120 mm length of tube is placed in the hottest zone of the furnace.

vi. Place the sample in the central portion between carbon or mullite rods with about 5mm thick carbon plates in between sample and rods.

vii. Apply the load of $2 kgf/cm^2$ is applied with the help of rods.

viii. Heat the furnace at the rate of $15^0C$ per minute up to $1000^0C$ and at the rate of $8^0C$ above $1000^0C$.

ix. Plot the change in height is against the time on rectangular co-ordinates. As the temperature is raised at approximately constant rate and change in height is plotted against the time , the chart will give temperature deformation curve.

x. Measure the temperature with the help of an optical pyrometer. It is sighted obliquely through a 20mm (max) ID radial tube or adjusted upon the bottom of refractory tube closed at its bottom and suspended in the furnace at the beginning of the test at about middle of the specimen . This is tightly closed by total reflecting prism interposed for giving allowance for diminution of intensity There should not be more than $30^OC$ variation in horizontal plane.

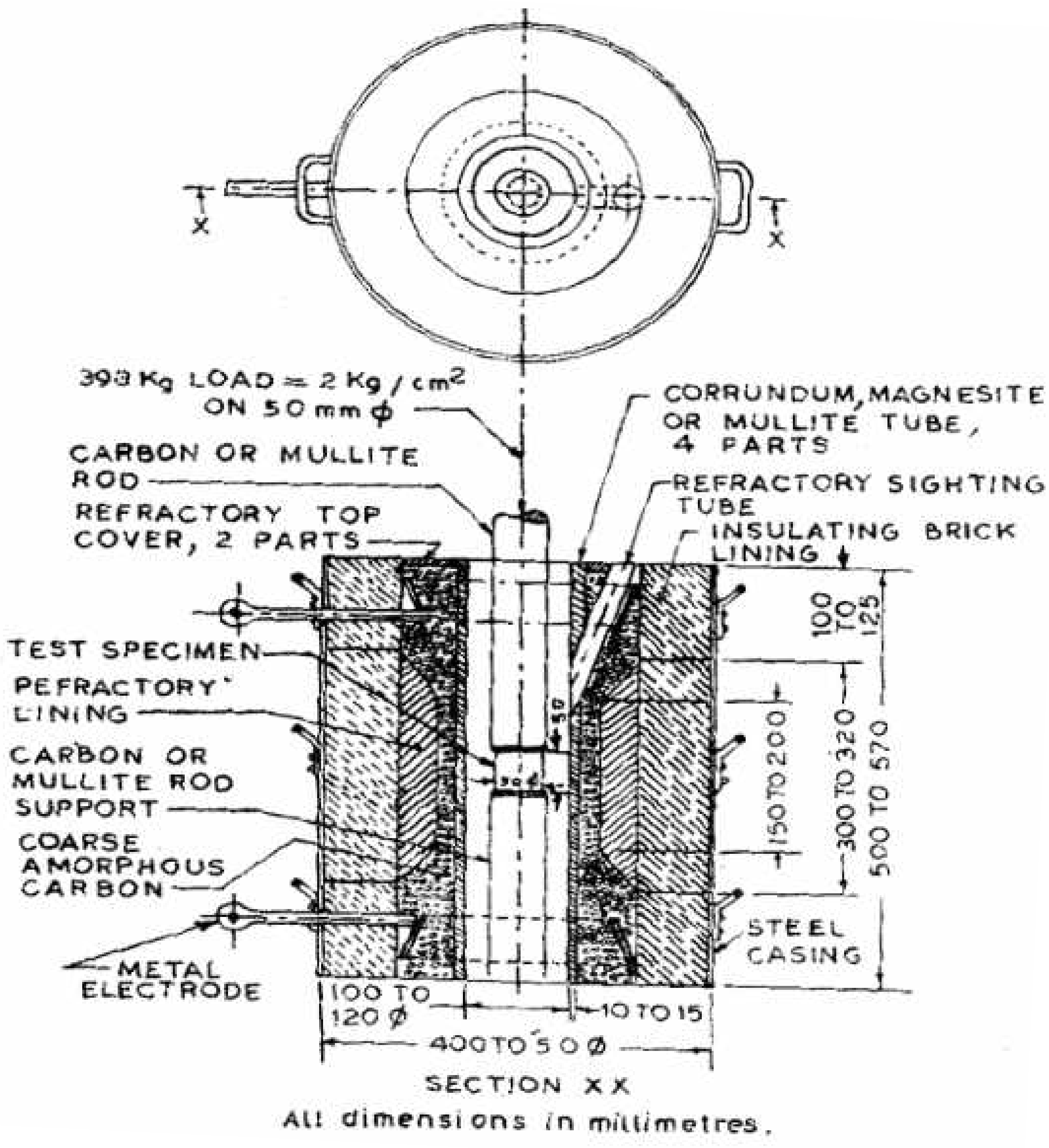


**Figure 5.5 RUL Furnace**

**(Reproduced from Refractories Manufacturing, Properties and Applications, Prentice Hall of India Private Limited, New-Delhi ,(1986)**

(xi) Change in the height of the specimen on heating is plotted against temperature on 10:1 scale to represent temperature deformation curve for the test. The typical curve for some of the refractories is shown in figure 5.6

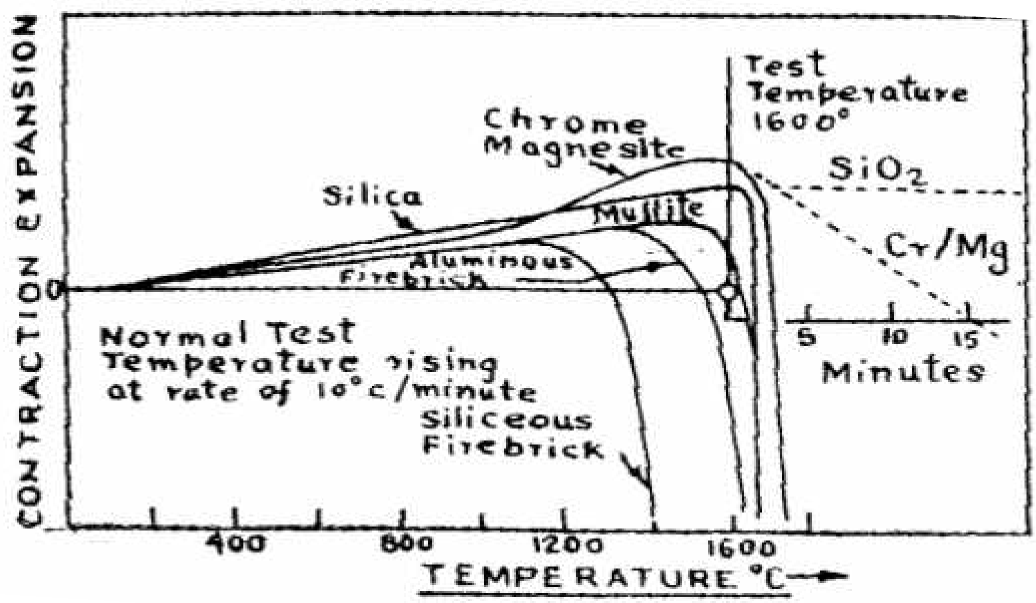


**Figure 5.6 Typical RUL curve of some of refractories.**

(xii) From the plotted curve, note the temperature ($T_a$) corresponding to the point at which the curve has dropped 3mm below its highest point( denoted by bend of curve downwards with respect to horizontal tangent).The temperature ($T_e$) cooresponding to the point at which the height of the tse specimen has decresed by 20mm from its original height is also noted. The temperature ($T_b$) at which premature breaking of the test specimen, without its actual softening takes place denotes the breking ponit of the test specimen.

### 1.5.3 Spalling resistance

Spalling resistance is determined by one of the two standards methods:-

1.5.3.1 Panel Test

1.5.3.2 Small prism test

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#### 1.5.3.1 Panel Test

**Procedure for determination of spalling resistance by Panel test method**

i. Cut 12 to 14 test specimens from original refractories by cutting wheel. The size of specimen should be of 65-70mm thick, 230 mm long and 113mm wide. If size of original brick is 230mm in length then take original shapes for testing.
ii. Label with ceramic paint on the inner face which is not exposed to heating.
iii. Each specimen is then dried at 105 and weighed.
iv. Then lay test specimens in the panel frame by kaolin or any other suitable material having PCE value not less than that of refractory specimen. Selected Material should not react with refractory specimens.
v. Ensure Joints of specimens less than 2mm thick.
vi. Back the test panels are with suitable insulation to allow heat loss of approximately 605 kcal/$m^2$/hr ($^oC$/m) under operating conditions. Its mean temperature should be about 700 $^oC$.
vii. Preheat the panel assembly gas or oil fired furnace. Maintain face temperature at 1600 (average) for 24 hrs. Raise the temperature of preheating i.e. up to 1600 in 5 to 8 hrs.
viii. Record the condition of samples after preheating and take photograph for record.
ix. Remove the insulation from panel and transfer the samples in spalling furnace with the help of track or trolley.
x. Heat the samples in spalling furnace at 1400 . Maintain the rate of heating in such a way that this temperature is attained in 3 hrs.
xi. Change the position of panels at 1000 , 1200 and 1300 for uniform heating. Heat the

specimens for 10 min. at 1400 .

- xii. Cool the panel cooled for 10 min. with the help of blast of air-water mist. This is delivered through vertical manifold having aperture of size 90mm × 600mm. Admit the air at the rate of 40$m^3$ per minute. Admit the water at rate of 11 litres during first 8 minutes of cooling. No water is admitted during last 2 minutes. The cooling unit is provided to and fro motion (about 125 times in one minute) over the entire surface of panel by external means.
- xiii. Subject the samples are subjected to such 12 heating and cooling cycles.
- xiv. Switch off the furnace
- xv. Subject the panels to another two cooling cycles without water mist

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- xvi. Then cool the specimen overnight after spacing the panel 25mm face to face
- xvii. Carefully remove the refractories samples after 24 hrs from the panel .
- xviii. Weigh all the samples and rearrange in original order for comparison with photographs. The average loss of weight of panel gives the indication of the extent of spalling resistance.

**1.5.3.2 Small prism test:-** This is another method to determine spalling resistance. The procedure is described below.

**Procedure for determination of spalling resistance by small prism test method**

- i. Cut three specimens from refractories(of standard shape) under test. Ground the specimens in shape of prism of size 50mm side and 75 mm height. In case of non-standard shapes (sleeves, nozzles or other pouring type refractories), the test specimens are cut in form of ring of height 50mm.
- ii. Dry these specimens to a constant weight.
- iii. Then place the specimens in cold muffle or semi-muffle type furnace. Heat the furnace at uniform rate to attain temperature of 450 in 3 hrs in case of silica refractories. In case of fireclay, siliceous or basic refractories heat the specimens to attain 1000 in three hours.
- iv. Heat the specimens for ten minutes.
- v. Remove the specimens from furnace with the help of pre-warmed pair of tongs.

vi. Place these specimens on a brick floor for 10 minutes for cooling. The room should be free from draughts.
vii. Observe the samples for any crack.
viii. Again reheat the specimens for 10 minutes and cool for another 10 minutes.
ix. Again observe the specimens for any cracks.
x. Repeat the steps eighth and ninth till cracks are appeared. Note the cycle, in which crack appear. Number of such heating and cooling cycles is the measure of spalling resistance

.

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## 2.5.4. Resistance to chemical attack

Chemical attack on refractories takes place due to slags, gases like carbon monoxide and glasses etc. at the high working temperature.

**2.5.4.1 Resistance to slag attack:-**

The resistance to slag attack can be determined by one of the following methods:-

**Running slag test:-** In this test specimen refractories in the form of single brick or column of bricks are heated to a uniform temperature. The temperature is near to the temperature at which refractory is finally to be used. Then the powdered slag dropped regularly on top of refractory. The slag run from here in groove downward provided for the purpose. At the close of test the depth of groove is again determined. The enlargement of groove determines the resistance of the refractory to slag attack. This test gives excellent results. However, this test can not be used to determine quantitative results.

**Spray test:-** In this test refractory sample is maintained at uniform temperature. The powdered slag is then sprayed on heated refractory surface with the help of revolving burner.

The slag powder is thus impinged uniformly and under similar temperature and other working conditions over the entire surface of the refractory under test. The decrease in thickness gives the slag resistance.

**Molten bath slag test:-** This is another test to determine the slag resistance. In this test the refractory to be tested is kept in bath of molten slag. The slag is stirred to expose the refractory surface to fresh slag. The decrease in dimension of brick gives the measure of slag resistance.

**2.5.4.2 Resistance to carbon monoxide attack:-**

Carbon monoxide have disintegration effect on refractories. This effect depends on amount of ferric oxide present in refractories. The carbon monoxide gas is generated by reaction of formic and sulphuric acid or by the reaction of charcoal at 1000 . You must purify the nitrogen and carbon monoxide for carbon, oxygen and water vapors. Measure



the flow rate carbon mono oxide with the help of manometer and a flow meter in the circuit.

**Procedure for determination of resistance to carbon mono oxide attack**

i. Cut two specimens cut in cylindrical shapes of 50 mm length and not less than 30 mm diameter. One specimen is cut from interior of refractories and other from exterior of other refractory shape. You can cut specimens in prismatic or rectangular shape.
ii. Place the test specimens in wire wound electrical furnace.
iii. Purge the furnace with nitrogen.
iv. Heat the furnace at 450 and pass purified carbon monoxide through the furnace at the rate of 2 litres per second.
v. Carry out the test for 100 hrs or when refractory gets disintegrated if it occurs earlier. Examine the test pieces regularly for discoloration, carbon deposition and disintegration that may take place during the course of test.
vi. Record the observations for each of the two specimens.
vii. Maintain the test temperature between 450 to 500 .

viii. Note the time at which disintegration or deposition of carbon monoxide takes place. This is taken as measure of resistance of refractory to carbon monoxide.

## 1.5.5 Permeability:-

It is a measure of rate at which a fluid flows through a porous body. It is denoted by the volume of gas or air in cc that passes through one centimeter refractory cube at a unit pressure difference(gm/cm sq.) per minute. Schematic representation of the permeability determination apparatus is shown in figure 5.7

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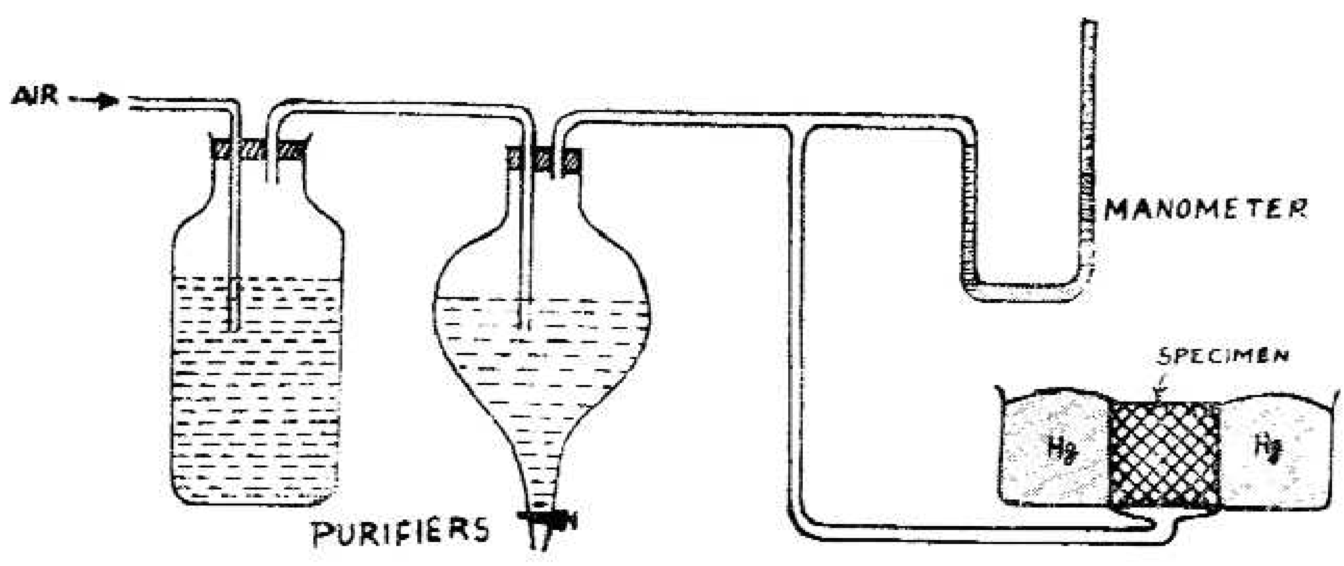

**Figure 5.7: Permeability apparatus**

Pass the purified air through a cubic refractory sample of known surface area and thickness. Fix the sample in mercury seal. The pressure difference is measured by manometer. Note the Volume of air passed in a given time. Then Permeability of refractory sample can be calculated by using the following formula:-

$$\textbf{Permability} = \frac{V.H.}{A.\ t.\ \Delta p}$$

Where V= Volume of air passed through specimen(cc)

H= thickness of sample(cm)

A= cross sectional area of the sample(sq.cm)

t= time for which air is passed through the sample(min)

Δp= pressure difference across the two surfaces of vthe sample(gm/sq.cm)

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## Now do the following practice task

1. Write the dimensions of the cones used in refractoriness testing.

2. What is P.C.E.

3 Write refractoriness value of silica brick.

4. Define RUL.

5. Write the size of refractory tube of RUL furnace?

6. Name the two  tests  used to measure resistance to slag attack.

7. Name the tests used to determine spalling resistance

8 .Why sample is sealed in mercury in permeability test.

.

NOW CHECK YOUR RESPONSE

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## FEEDBACK TO THE PRACTICE TASK

1. Tetrahedron shape with base side 8mm, Height 25mm

2. Pyrometric cone equivalent

3. 1710 degree Celsius

4. RUL means refractoriness under load .It is a measure of a resistance of a refractory product to deformation when it is subjected to combined effect of load, heat and time.

5. Internal diameter = 100 to 120 mm,

   Outer diameter =120 to 150 mm

   Length = 500 mm

6. (i) Running slag test

   (ii) Spray test

7. (i) Panel Test (ii) Small prism test

8. Since mercury is not wetting and also it make the sides completely air tight so that fluid can pass through only opposite faces

# UNIT V B  Testing of Refractories

**OBJECTIVES**

GENERAL OBJECTIVE: Understand the methods of testing refractories.

SPECIFIC OBJECTIVES: At the end of this unit, you will be able to

1. Describe steps involved in testing apparent porosity
2. Describe method of testing bulk density
3. Describe method of testing true specific gravity and true density.
4. Describe method of testing modulus of rupture.
5. Describe method of testing permanent linear change.

# INPUT

## 2.5.6 Apparent porosity

You can determine the apparent porosity by any of the two methods

### 2.5.6.1 Boling point method

This test takes the following procedural steps

i. Cut the test specimens of size 6.5cm×6.5cm×4cm with the help of cutting wheel. The sample should be cut from interior of the brick
ii. Remove the any loose adhering particles.
iii. Dry the sample in oven at 110 to a constant weight. Note it as ‘D’.
iv. Suspend dry sample in distilled water. The sample should not touch sides or bottom of the vessel.
v. Boil the specimen in suspended condition for two hrs and the cool it.
vi. Take its weight in suspended condition and note it as ‘S’.
vii. Remove the specimen from water.
viii. Wipe of extra water with blotting paper
ix. Weigh in air and note it as ‘W’
x. Then calculate apparent porosity (P) by using following formula: -

$$P=\frac{W-D}{W-S}\times 100$$

Where W-D= actual volume of open pores of the specimen (CC)

W-S= external volume of the specimen (CC)

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### 2.5.6.2 Evacuation method

You can determine the apparent porosity by evacuation method also.

Following are the steps to carry out the test

i. Cut the test specimens of size 6.5cm×6.5cm×4cm with the help of cutting wheel.
ii. Cut the sample from interior of the brick and remove any loose adhering particles.
iii. Dry the sample in oven at 110 to a constant weight. Note this weight asdry weight 'D'.
iv. Place the dried sample in empty vaccum desicator.
v. Evacuate the desicator to a pressure less than 25 mm of Hg.
vi. Then admit the immersion liquid (water or farction of liquid paraffin boiling above 200 ).
vii. Place the sample in such condition for 2-3 hrs under reduced pressure.
viii. Allow the air to enter the desicator.
ix. Take its weight in suspended condition with the help of sling thread.Note it as suspended
weight 'S'
x. Remove the specimen with the help of sling thread slowly. Wipe of extra water with blotting paper
xi. Weigh in air and note it as saturated weight 'W'.
xii. Then calculate apparent porosity (P) by using following formula: -

$$P = \frac{W-D}{W-S} \times 100$$

Where W-D= actual volume of open pores of the specimen (CC)

W-S= external volume of the specimen (CC)

**2.5.7 Bulk Density**

Bulk density can be measured by either of two mwthods

2.5.7.1. Direct measurement method

2.5.7.2 Direct volume measurement method

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**2.5.7.1 Direct measurement method:-**

This method is used to determine the bulk density of regular shape refractories.First determine the volume of refractories by measuring its dimensions directly. Then take its weight. The bulk density is then determined from the formula:-

$$D_B = \frac{W}{V} \text{ (g/cc)}$$

Where W = weight of specimen in grams

V= volume of specimen in cc.

**2.5.7.2 Direct volume measurement method:-**

This method is used to determine the bulk density of those refvractories which are having intricate shapes.In this method value of dry weight(D), suspended weight(S) and saturated weight(W) is determined. The same procedure is used , which was used for apparent porosity determination. Then calculate the bulk density by using the following formula:-

$$D_B = \frac{D}{W-S} \text{ (g/cc)}$$

Where D = Dry weight of sample(in gram)

w-s = external volume of specimen( in cc)

#### 2.5.8 True Specific Gravity and True density

This test is conduvted when materials does not dissolve in or attacked by water.

Procedure for detrimination of True specific gravity and true density.

i. Take two test specimens of refractory to be tested
ii. Cut two test pieceses of walnut size from interior of refractory
iii. Crush the piecese to a size not exceeding 3 mm.
iv. Mix and reduce the crushed sample to 50 gram by coning and quartering
v. In case of pre ground material, draw 500 gram of representative sample and reduce to 5o gram by coning and quartering.
vi. Grind cone mateial in agate so that it pass through 149 micron IS sieve.
vii. Remove magnetic fractions with the help of magnetic seperator introduced during crushing and grinding.
viii. Dry the material to constant weight at 105-110 $^{O}$C
ix. Take 8-12 gram of sample and place in glass stoppered weighing bottle.
x. Take a pycnometer dry it at 105-110 $^{O}$C,cool in dessicator and note down its weight as 'Wp'
xi. Fiil the pycnometer with distilled water at room temperature.
xii. Place the stopper
xiii. Wipe the extra water outside and note down its weight as '$W_1$'
xiv. Empty the pycnometer, dry it and fill with material sample from weighing bottle. Weight it and note it as 'W' with stopper in position.

xv. Fill half of pycnometer with distilled water and boil it for 10-15 minutes. This is done to avoid loss of sample due to popping.

xvi. Then fill the remaining part of pycnometer with distilled water and cool to room temperature in water bath.

xvii. Place th stopper in position and wipe of extra water.

xviii. Weigh the pycnometer and note its weight as '$W_2$'

xix. Calculate specific gravity and true density by using following formula

$$\text{True Specific Gravity} = \frac{\text{weight of sample}}{\text{weight of equal volume of water}}$$

$$= \frac{W - Wp}{W - Wp\ - (W2 - W1)}$$

True density = True specific gravity × ($d_w$-$d_a$) g/cc

$$= \frac{(W - Wp)(\mathrm{dw} - \mathrm{da})}{W - Wp\ - (W2 - W1)}\ \text{g/cc}$$

Where $d_{w\ \text{and}}$ $d_a$ are densities of water and air repectively at the temperature at which test is conducted.

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## 2.5.9 Cold crushing strength:-

Do you know importance of this test ? This is so because refractories bricks are subjected to load bearing services. CCS is determined by standard hydraulic or mechanical compression testing machine shown in figure 5.8 .Various steps involved are

(i) Cut the test specimens from refractory shapes preserving the original surface as far as possible. Size shuld be kept equivalent to size of 230mm standard brick.If smaller and other special refractory shapes the test specimens the smaller size are used. In this case sample size can be cube with side of 75mm are used.

(ii) Keep the specimens between two rams(bearing block having plane surface of size equal to or more than that of specimen) of machine. In betweenram and specimen 5mm thick asbestos fibre board or cardboards are kept. As shown in figure 5.8.

(iii) Switch on the machine to move the rams. The machine indicate the pressure in terms of tonnage on pressure gauge. The pressure will be shown for every moment.

(iv) Note down the pressure when the brick fails.At this point indicator returned back to zero.This value of machine gives the value of CCS. At the time of failure, cracks will apear on the surface of sample.

The assembly used in test is shown in figure 5.8:-

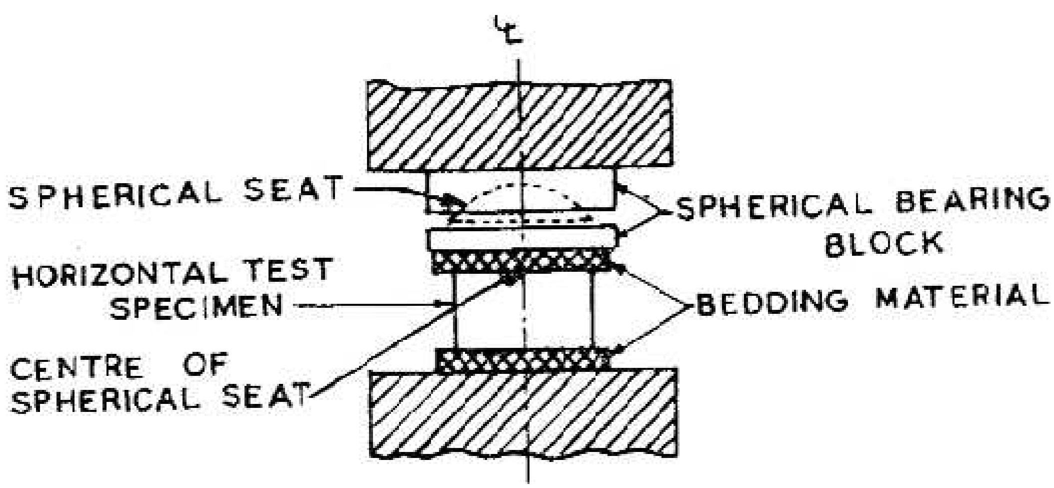


**Figure 5.8 Crushing test assembly**

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**2.5.10 Permeability:-**

It is the measure of the rate at which the fluid flows through a porous body. It is denoted by the volume of gas or air in cc that passes through one centimeter refractory cube at a unit pressure difference(g/cm2). The schematic representaion of the permeability appartus is shown in figure 5.9

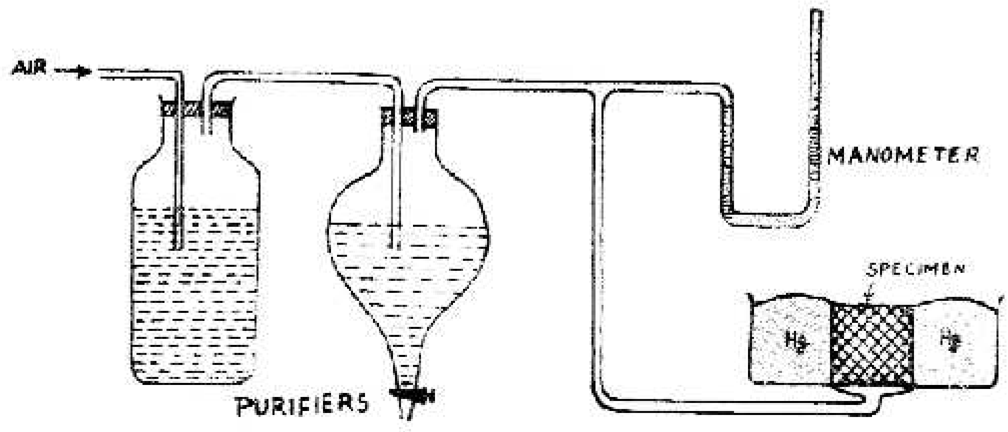


**Figure 5.9: Permeability appartus**

In this test pass the purified air through a refractory sample of known surface area and thickness. The sample is fixed in a holder with a mercury seal. The pressure difference is

measured by a manometer. Note the volume of air passed in a given time. Permeability of refractory sample is calculated by using following formula:-

$$\text{Permeability} = \frac{V.H.}{A.t.\Delta p}$$

Where V= volume of air passed through specimen (cc)

H= thickness of specimen(cm)

A = cross sectional area of the specimen(sq. cm)

t = time for which air is passed through specimen(min.)

Δp= pressure difference across the two surfaces of the sample(g/sq.cm)

**2.5.11 Modulus of rupture test (MOR)**

Failure of refractory brick generally takes place due to bending moments. In practice failure of bricks due to crushing rarely takes place. MOR test is used to determine resistance offered by brick to bending moments. This test is performed with the help of standard mechanical or hydraulic compression machine as shown below:-

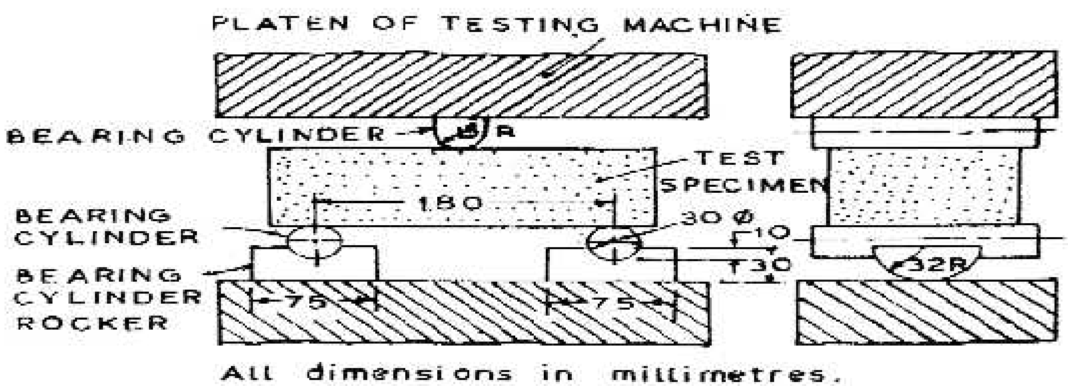


**Figure 5.10: MOR machine**

To perform this test cut the test specimen of size 22cm×11.3 cm×6.5cm or 7.5cm. The specimen is cut from desired refrcatory shape. Place the specimen on the bearing edges of the machine.These edges are positioned 18 cm apart. Apply the load at the middle of the specimen uniformly. The rate should be 10kgf per minute(±10%) in case of mechanical

pressing machine. Load shiuld be applied without any jerk. Note the load (W) at which the specimen fails. Then use following relation to calculate MOR.

M.O.R. = $\frac{3WL}{2bt2}$ kgf/sq. cm

Where L = the distance between bearing edges(cm)

b= width of specimen(cm)

t= thickness of specimen(cm)

**2.5.12 Permanent linear change (PLC)**

Do you know why permanent linear cahnge is important to determine? Because it indicates the volume stability i.e, expansion or shrinkage, of the refractories takes place during service( use as lining). It also indicates reversible thermal expansion i.e., the



material expands on heating and contract on cooling due to phase transformation during use. The PLC and reversible thermal expansion value is used in designing refractory lining for providing expansion joints.PLC is can be determined by two methods.

**2.5.12.1 Permanent linear cahange on reheating(PLCR) :-**

This test is carried out in the laboratry furnace. The sample is heated to particular temperature for particular time. This temperature and time is different for dirfferent refracory materials. The test results can be reported in two ways

**Linear change:-** The PLCR is expressed as percentage of increase/decrease in length as under

$$\text{PLCR \%(linear)} = \frac{\text{Increse/decrease in length}}{\text{original length}} \times 100$$

**Volumetric change:-** The PLCR can also be expressed as percentage of increase/decrease in volume as under

$$\text{PLCR \%(volume)} = \frac{\text{Increase/decrease in volume}}{\text{original volume}} \times 100$$

**Procedure to determine PLCR**

i. Cut the test specimen of size 5×5×12.5 cm by cutting wheel.In case of smaller refrcatory shapes, the specimen of largest possible size is cut. Retain maximum possible original faces.

ii. Determine its volume and Place it in kiln having oxidising atmosphere.Keep the specimen in such a way that flame does not impinge directly on specimen. The largest face of the specimen should rest on a supporting refractory brick drawn from same lot of refractories that are under test.

iii. Place fused alumina or kyanite of – 85 micron I.S.sieve between supporting refrcatory and test specimen. Keep the specimens 4cm apart.

iv. Heat the test specimen according to set time-temperature schedule of particular refractory.

v. Hold the refractory for given time at maximum temperature as per stipulated time.

vi. Cool the refractory specimen in the kiln itself in 10 hours.

vii. Measure its dimensions again and calulate its volume.

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ix Calculate PLCR by using following formula:-

$$\text{PLCR \%(linear)} = \frac{\text{Final length} - \text{original length}}{\text{original length}} \times 100$$

$$\text{PLCR \%(volume)} = \frac{\text{Final volume} - \text{original volume}}{\text{Original volume}} \times 100$$

**2.5.12.2 Dialtometer method of testing PLC:-**

This is method is used to measure linear change of refractory sample with temperature. Dialtometer assembly is shown in figure 5.11

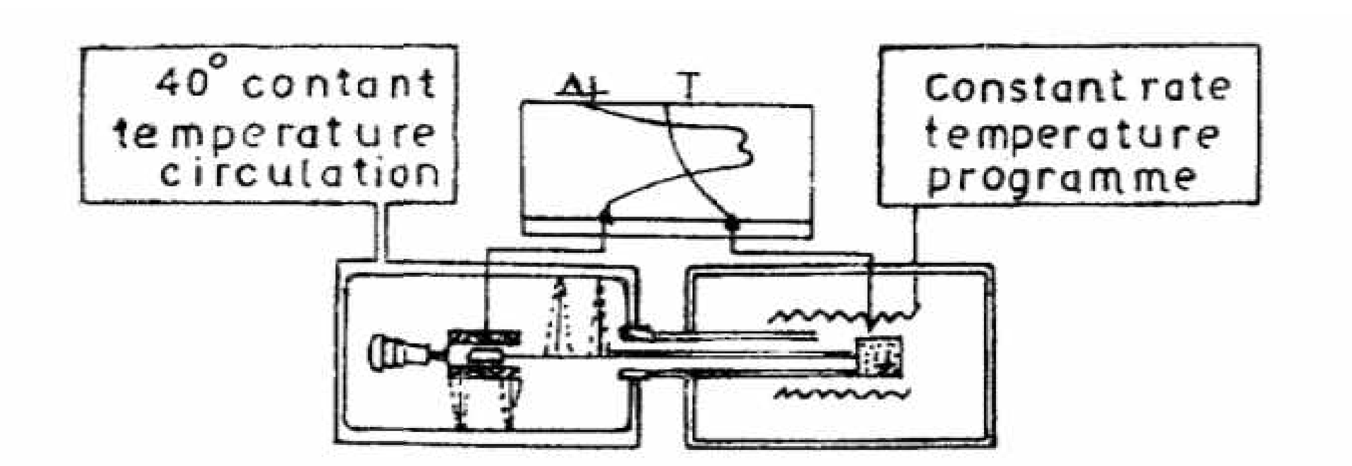


**Figure 5.11 Dialtometer Assembly**

In this test a sample is cut in shape of cylinder or bar. Clean the sample from any loose dust particles. Place the cut specimens on supporting tube in such a way that its other end is free to expand. This free end is joined to core of an electronic displaement transducer. When sample is heated change in length takes place. This makes the free end to move and which in turn pushes the ceramic rod. This rod pushes the core of the trandsducer. Record the deflection in millivolt. This deflection is proportional to the change in length of specimen. Time to time standardisation of dialtometer is done with the help of material of known coefficient of thermal expansion. From this correction factor is determined forr expansion which takes place in ceramic tube and carrier

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refractory on heating along with specimen. Dialtometric analysis enables you to determine structural changes and percentage of different phases formed due to transformaton on heating. These changes involve changes in volume e.g. % of cristballite,tridymite and quartz in a silica brick on heating to desired temperature.

**2.5.12 Expansion characterstics:-**

Expansion characterstics is very important property for the refractories. It is very essential to know about refractories whether it will expand or contract during heating ensures the stability of it.

Expanding refrcatories are not suitable for the most applications. Expansion sets up stress causing blowing and bursting of lining.Firebrick, chrome magnesite, forsterite, magnesite and alumino silicate refractories shrink in service. Silica refractories expand on heating due to critical transformation.Expansion of refracatories depends on composition and temperature. Expansion of refrcatory also varies from batch to batch and brick to brick. Ordinary or thermal expansion value is very impotnat in furnace design.This helps for providing expansion joints. Expansion factor also determine thermal shock resistance.

Firebricks have low and uniform expansion up to 1000□ . The ≤ 0.5% or less.Silica bricks behave differently. Tridymite shows two irregularties , while cristoballite and quartz shows one irregulaty in thermal expansion as shown in following figure.

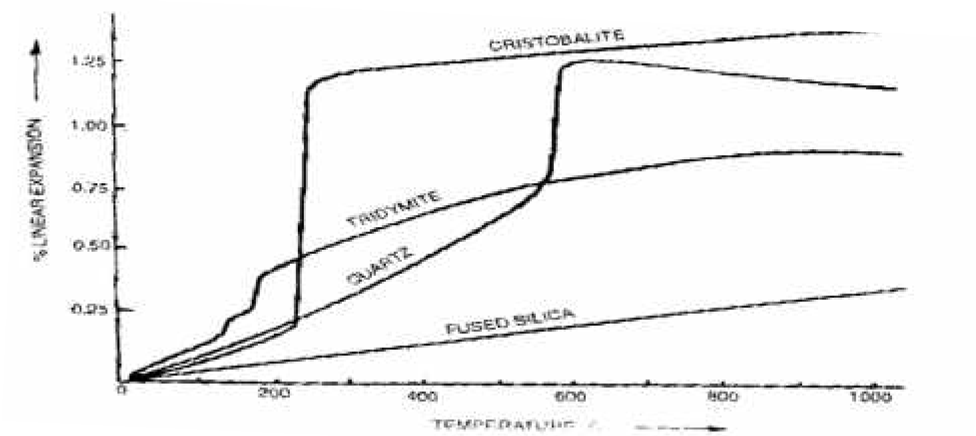


**Figure 5.12: Expansion of silica minerals**

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The thermal expansion of magnesite refractory is comparitively high 1.3-1.4% where as that of chrome or chrome magnesite brick is much lower except in reducing atmosphere. Normal fireclay refractories have low thhermal expansion of the order of 0.5% up tp 1000□ . Reversible thermal expansion of some refrcatories is shown in following figure 5.13

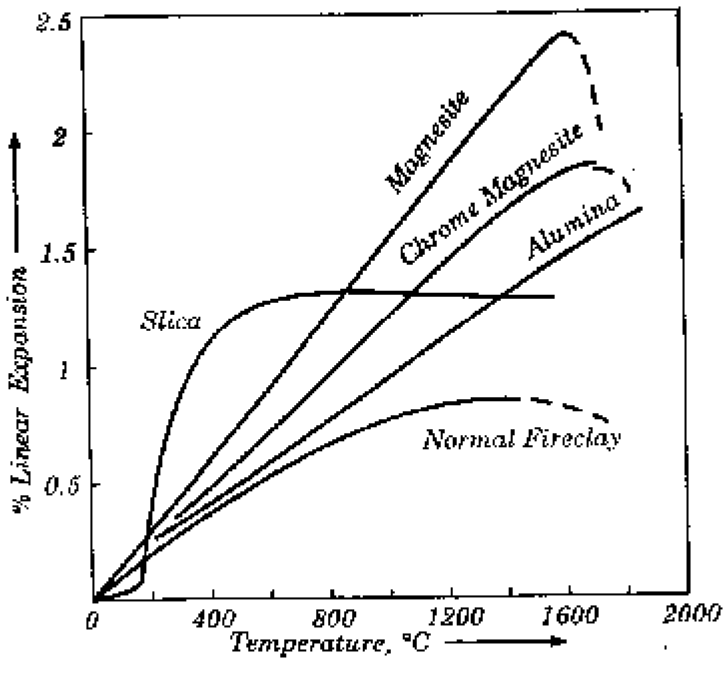


**Figure 5.13: Expansion Curve of some refractories**

**2.5.13 Thermal coductivity test:-**

Thermal conductivity depends on chemical and mineralogical comoposition, glassy phase and application temperature.It does not affect performance but its value determine the thickness of lining. Can you guess what should be it's value high or low?. Well it depends on application. In some application its value should be high e.g.in recuperators, regenerators, muffles etc, where heat transfer is required. However where heat conservation is required its value should be low. Thermal conductivity can be determined by calorimetric method developed by CGCRI calcutta as shown in following figure 5.14.

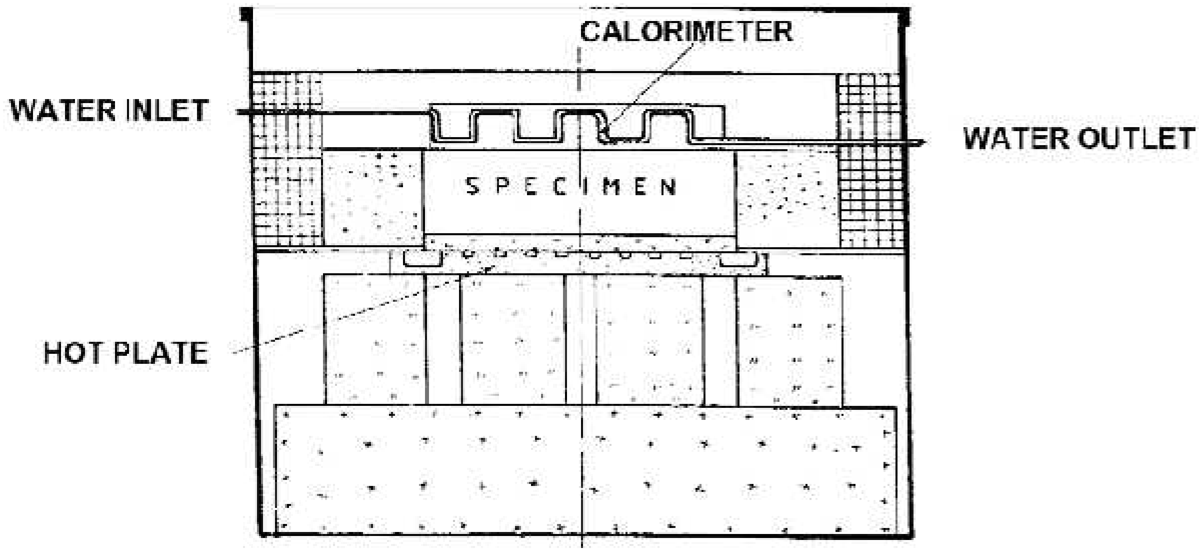


**Figure 5.14 Thermal conductivity apparatus**

This method was develpoed by C.G.C.R.I. Calcutta.This method is very useful for measurement of conductivity at very low temperature.This method was specifically useful for measurement of thermal conductivity of cold face(low temperature) low insulation bricks.In this method one end of brick is heated with the help of hot plate. At the other end water is circulated through calorimeter. The inlet and outlet temperature is measured. This gives the rate of heat transfer passing through brick. The water flow is so adjusted such that the temperature of cold end is constant.

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**Now do the following practice task**

1. Define the apparent porosity.

2. Write the formula used to calculate bulk density.

3. Explain determination of  MOR.

4. Name the testing method used to find density and porosity of irregular shapes

5. Explain determination of  the bulk density

6  Name the test used to measure PLCR.

7. Write the formula used to calculate permeability of refractory sample.

NOW CHECK YOUR RESPONSE



**FEEDBACK TO THE PRACTICE TASK**

1. Apparent porosity is expressed as percentage of open pore space to the total refractory volume.

2. Bulk Densiry = $\frac{D}{W-S} \times 100$

where D = the constant weight of the Dry Sample

S = the weight of specimen suspended in water

W = the weight of specimen in air including the moisture in

open pores.

3. Failure of refractory brick generally takes place due to bending moments. MOR test is used to determine resistance offered by brick to bending moments. This test is performed with the help of standard mechanical or hydraulic compression machine. To perform this test cut the test specimen of size 22cm×11.3 cm×6.5cm or 7.5cm. The specimen is cut from desired refrcatory shape. Place the specimen on the bearing edges of the machine.These edges are positioned 18 cm apart. Apply the load at the middle of the specimen uniformly. The rate should be 10kgf per minute(±10%) in case of mechanical

pressing machine. Load shiuld be applied without any jerk. Note the load (W) at which the specimen fails. Then use following relation to calculate MOR.

M.O.R. = $\frac{3WL}{2bt2}$ kgf/sq. cm

Where L = the distance between bearing edges(cm)

b= width of specimen(cm)

t= thickness of specimen(cm)

4. Boiling point Method and evacuation method.

5. Bulk density can be measured by

**(a) Direct measurement method:-**

This method is used to determine the bulk density of regular shape refractories. First determine the volume of refractories by measuring its dimensions directly. Then



take its eight. The bulk density is then determined from the formula:-

$D_B = \frac{W}{V}$ (g/cc)

Where w = weight of specimen in grams

v= volume of specimen in cc.

**(b) Direct volume measurement method:-**

This method is used to determine the bulk density of those refvractories which are having intricate shapes.In this method value of dry weight(D), suspended weight(S) and saturated weight is determined. The same procedure is used , which was used for apparent porosity determination. Then calculate the bulk density by using the following formula:-

$D_B = \frac{D}{W-S}$ (g/cc)

Where D = Dry weight of sample(in gram)

w-s = external volume of specimen( in cc)

6. Dialtometer test

7. Permeability = $\frac{V.H.}{A.t.\Delta p}$

Where V= volume of air passed through specimen (cc)

H= thickness of specimen(cm)

A = cross sectional area of the specimen(sq. cm)

t = time for which air is passed through specimen(min.)

Δp= pressure difference across the two surfaces of the sample(g/sq.cm)

# UNIT -3

1. **Fire Clay Refractories –** fireclay are hydrated alumino silicates represented by a12O3.2SIO2.2H2O at higher temperature water is driven out. The chemical composition of fireclay is 25-45% AI203 and 50-80% SIO2. Fireclays may be plastic, semi-plastic or non-plastic. Flint clays are very hard and non plastic; its plasticity can be increased by addition of bond clay to them.

   Plastic clays may be less refractory and hence their refractories is increased by the addition of more refractory clay thus desired properties of the fireclays are achieved by mixing different clay in proper proportions.

   Fireclays fuses between 1580-1750.c,presence of alkalies,sand,gravel,calciumcarbonate,monoxide,calciumsillate,magne sumsilicate,ironsillicate,magnesiumcarbonate,ironsulphite etc in fireclays seriously lower their fusion temperature and therefore should be free from them as far as possible.

Alkalis and basic oxide are most harmful elements because they from doubles silicates of lower refractories.

**PREPARATION-** Clay got from the mines, is left in the open in thin layers for weeks or months. This causes the decaying of organic matter present in the clay due to heat, cold and atmospheric moisture. Some organic acids thus produced increase the plastically of clay. This treatment is called "weathering of clay" or" souring". Weathered clays are crushed by gyratory crushers and ground in edge runners. The finely crushed clay is then mixed with grog.

Artificial weathering and even partial drying of clays is also carried out in some specific case using rotary driers.

Grog, is a term used for fired clay particles. A good refractory clay is hard fired in rotary kilns and crushed to desired particle size. It is also made by crushing previously fired broken and scrap bricks. Grog is added to the clay mainly as an anti-shrinkage elements in the form of angular particles of various sizes to achieve better interlocking of grains.

Grog is added to clay for the following advantages-

1. Less shrinking on heating.
2. Increased strength of the fired refractories.
3. Decrease apparent porosity and increased specific gravity.
4. Greater resistance to sudden changes in temperature.
5. Less addition of water to get a workable plastically and lesser time required for drying the raw refractories and hence increased rate of production.
6. Ordinary and low grog fireclay refractories contain 20-40% grog and high percentages, of the order of 60-80% of raw clays having high porosity and low strength, high shrinkage. Use of higher percentage of grog results in high heat duty and improved properties in the final product. High grog fireclay refractories contain upto 90% grog and low percentage 10-15% of raw highly plastic clay to impact necessary binding properties. Quality of high grog products can be improved by use of:-

1. Fine dispersion and through tempering of highly plastic bond clay to ensure its proper distribution and effective binding by as thin layers of clay as possible.

2. Calcined material of high grain density for improved strength and soundness of the product.
3. Properly graded raw materials in the mixture to ensure highest packing density and reduction and mixed.

**MIXING-** Finely crushed refractory clay is mixed with an appropriate quality of the prepared grog. If necessary, with the bond clay or Calcined bauxite. Mixing is carried out either in dry state or by wet methods. In the former case different ingredients are taken in requisite proportions and mixed.

In wet mixing the ingredients are mixed with water in pug or pan mill. The mixture may be allowed to mature for a number of days in a cool cellar before moulding to increase its plasticity.

**MOULDING/SHAPING-** Moulding is carried out either by hand moulding, pneumatic ramming or by mechanical pressing. About 7-9% water is used in hand moulding mixtures and 4-7% water in case of machine moulding mixtures. Lower moisture content in mixtures requires high moulding pressure and higher moisture containing mixes increase the slumping chances at the time of release from the mould.

Hand moulded refractories may not be of the appropriate sizes and may be less than those produced by machine- moulding processes may be rotating table, friction screw, jolting, hydraulic and toggle type. Other methods of moulding include extrusion wire cutting and re-pressing. Special shapes like are made by extrusion followed by re-pressing. Mixture used for shaping by extrusion use as high as 15-20% moisture and therefore extruded shapes need special attention while drying to avoid formation of cracks and other defects.

**DRYING-** Drying of moulded shapes is done under shade or in well ventilated rooms and in absence of direct sunshine as faster rate of drying will result in crack formation. Faster rate of drying results in uneven drying and development of student in the refractory shapes making them liable to crack.

Slow rate of drying ensures uniforms drying both inside and outside the compact mass. Thus drying is carried out quite cautiously under predetermined condition of temperature and humidity. Steam heated floors are used for final drying of green hand moulded or extruded products after 1-4 days natural drying. Drying is also carried out in conditions tunnel type dryers where cars loaded with moulded shapes are pushed at a uniform rate. Hot air at 150 to 250.c is introduced form the discharge end which leaves the dryer at 60. To 80.C at the charging end.

In cold countries, humidity controlled dryers heated by flue gases from furnaces are employed for drying purpose. Drying period may very form 24 to 200 hours depending upon the composition, method of moulding and size of the products.

**Firing-** firing of dried fireclay refractories is carried out in batch or continuous type kilns. The kilns may be downdraught, up-draught or horizontal draught type. Tunnel kilns are used for mass production and chamber kiln are generally preferred for larger and complicated shapes. Burning of fireclay refractories may be divided into five stages depending upon the temperature of the furnace and the changes that take place in the dried refractories.

First stage is known as “steaming”. Expansion of any water or moisture which has been left in the material after drying take place in this stage.

Second stage is said to be begin after a temperature of about 350.c has been reached and extends up to 900.c. it last for about 20 hours and results in decomposition of clay. Any molecular water present is driven out and the combustible and volatile matter is also expelled. This stage is also known as “smoking”.

Third stage is known as “oxidation” or “full fire stage”, last for about 12-36 hours and extends up to a temperature of 1350.c permitting various mineral transformation. At a temperature of about 950.c alumina begins to combine with silica to form mullite ($3Al_2O_3.2SiO_2$) and this is accompanied by evolution of heat. It being to an exothermic reaction. Crystallization of mullite is completed between 1350-1380.c. The clay shrinks and gets hardened and no shrinkage of the refractories takes place on subsequent heating or when in use.

Fourth stage is also known as the stage of “incipient fusion” extends up to 1500.c and is accompanied by the incipient fusion of the impurities and filling up of the interstices between the solid particles by fused mass. Burning is finished at temperature higher than that at which the refractories are to be used.

Fifth or the final stage is known as “annealing and cooling”. This involves in very slow cooling of the fired refractories in the fired refractories in the kiln itself. In batch type kilns, the fire is put off and the damper closed and heat is lost by radiation. The cooling takes about the same time as heating the goods to the maturing temperature. In continuous kilns cooling takes place as the fired refractories move towards the discharge end.

After burning, refractories are sorted and stored. Some of the bricks which are under-fired are fired again. Over fired or other defective refractories, like “black-heart” formed due to insufficient supply of oxygen for combustion in the kiln etc are rejected.

Properties-Properties of fireclay refractories depends on the proportion and type of clay and amount of alumina, grog and other constituents present in them properties are given below:-

1. Colour – colour varies from light buff to reddish buff depending upon the iron content of the raw material. The bricks made from china clay are white in color.
2. Durability (Slag attack) - Fire clay refractories are slightly acidic in nature, hence they are not resistance to the action basic slag’s, alkalis, molten fluxes etc. the finer the grain texture of refractories the better their resistance to the action of otherwise corrosive media.
3. Chemical activity- fireclay refractories combine with salts such as chlorides, sulphate and carbonates or bases like lime, magnesia, iron oxide , ash etc forming fusible aluminum, silicates and aluminosilicates.
4. Porosity- Porosity of fireclay refractories varies from 8-24% depending upon the grain fineness and the temperature of firing.
5. Thermal fatigue- fireclay refractories have a low co-efficient of thermal expansion and hence are resistant to thermal fatigue. Coarse textured and high grog containing refractories have a greater resistance to thermal fatigue than those produced from fine textured and low grog mixtures.
6. Refractories- Fireclay fuses between 1580-1750.C.
7. Refractoriness under load- Refractories under load depends on the chemical composition and physical structure of the material, presence of impurities like iron, alkalis etc has a marked effect on their Refractoriness under load. Fireclay refractories do not fall below 1350.c under a load of 2kgf/cm2.
8. Cold crushing strength- Cold crushing strength of these refractories is about 200-400 kg/cm2 depending on their composition, texture and firing temperature. Cold crushing strength of a wall fired refractory is higher than that of a soft fired refractory.

**APPLICATIONS-** Fireclay refractories are the most commonly used refractories because of their cheapness, since they are a lightly acidic in nature. Their use in basic conditions is avoided. They are extensively used for lining iron blast furnaces, hot blast stoves and cupolas. For their marked resistance to thermal fatigue, these refractories are used for regenerative furnaces.

Other applications of fireclay refractories include those in recuperater, annealing, roasting and furnaces, glass melting furnaces allowed to cool frequently. They are also extensively used for flues, chimney linings and in steel casting, pottery, cement, petrochemical and fertilizer industries etc.

2. **Silica refractories-** Silica used for the manufacture of Silica refractories exists in the form of quartz, a polymorphic form of silica.

Quartzite is the most used naturally available form of quartz employed for the manufacture of silica refractories in most countries.

India has plenty of quartzite deposits though however Biharsharif and Monghyr districts of Bihar and Lotapahar and Brajmada in Orissa containing about 98.5% $SiO_2$ with very small amounts of $Fe_2O_3$ and $Al_2O_3$ have been most used for Silica refractories manufacture. Other quartzite producing states include Karnataka and Madhya Pradesh.

Bonding of Silica grains is achieved by the addition of milk of lime in amounts of about 1-2% of CaO. This is serves as mineralizer include iron oxide, borax, oxides of magnesium and barium, fluorides, phosphates and carbonates of certain metal like sodium, lithium, potassium etc. This disadvantage of adding such elements is that they reduce the refractoriness of silica and hence should be added in minimum necessary amounts. Use of higher percentages of lime reduces the strength and resistance to abrasion of these refractories.

Addition of zircon to silica refractory materials improves their resistance to slag attack and however, zircon-quartzite refractories show lower compressive strength than quartzite or zircon materials.

Various steps involved in the manufacture of silica refractories are given below:-

1 **Raw quartzite-** Raw quartzite is washed to eliminate all the dust and other such impurities from it. It is then crushed in jaw or gyratory crushers and ground to desired fineness in bell mills. Fine, medium and coarse

grains are mixed in definite proportion and mixtures with following grain distribution have been found to result in high bulk density and a product with improved properties:-

| FRACTION | SIZE (mm) | PERCENTAGE |
|---|---|---|
| FINE | -0.2 | 45-50% |
| MEDIUM | -0.2-1.0 | 10-15% |
| COARSE | 1.0-3.0 | 35-40% |

2 **Mixing-** properly graded quartzite is mixed thoroughly with the desired amounts of the binding material and water to form a plastic mass. Mixing is done in revolving-bottom counter flow type mixers or pan mills. Wet mixing produces a uniform paste, plastic enough for moulding into different shapes.

3 **Moulding-** moulding of the semi dry mix, known as the tempered mass, is carried out either by hand or machine. Hand moulding may produces refractories of unequal hardness and density because of non-moulding ramming. Machine moulding is particularly advantageous for producing silica refractories of uniform density and high hardness. Shaping of heavy section is normally done by hand moulding. Refractories with high cold crushing strength, low porosity and high bulk density are produced by hydraulic pressing. Rotating table type presses though preferred for mass production of standard shapes, giving somewhat inferior quality product than that of friction presses.

4 **Drying-** Drying of pressed silica refractories is carried out in well ventilated rooms. As silica refractories are moulded out of a semi-dry mass containing a very low amount of water, they can be dried on hot floors/rooms to minimize the period of drying to less than 12 hours. Care is to be taken to eliminate uneven drying inside and outside the refractory shapes.

5 **Burning-** Burning of the silica refractories is done in batch type kilns. Careful handling of dried refractories is necessary as these are friable. Close setting of the refractories in the kiln avoided to accommodate their expansion on heating. These furnace are either gas-fired or coal-fires. The temperature of the furnace is slowly increased to about 1450-1500.C. This produces a maximum amount of cristoballite and tridymite. Uniformly of temperature in different parts of kiln is better achieved in smaller

downdraught kilns. The rate of heating and cooling particularly during the transformation must be very slow. Entry of cold air to the kiln during cooling is avoided by sealing its hearth.

**Properties-** the most prominent property of silica refractories is that their refractoriness under high loads.

I. **Colour-** Silica refractories have a white or buff colour depending upon the amount of bonding elements and mineralizers used.
II. **Specific gravity-** It varies from 2.3-2.35 depends on the temperature at which it has been burnt.
III. **Porosity-** Porosity of the silica refractories varies from about 22-26%.
IV. **Chemical activity-** except hydrofluoric and phosphoric acids, they are unaffected by all other acids. Acidic slag's have no action on these refractories. Hydrofluoric acid attacks silica in cold and phosphoric acid attacks in the hot (at about 400.C). Bases and alkalis including the oxides of iron, calcium and other metals attack silica particularly at high temperature forming complex and fusible silicates. Resistance to slag attack of silica refractories increase with increasing density but their resistance to spalling gets reduced.
V. **Refractoriness-** high quality silica refractories are highly refractory and have a fusion temperature of about 1710.C. This however, is greatly reduce when impurities are present in silica.
VI. **Refractoriness under load-** Silica refractories do not fall below 1650-1690.c under a load 2kgf/cm2 depending upon chemical composition of silica refractories.
VII. **Thermal shock resistance-** sudden changes in temperature disintegrate silica refractories due to the formation of fine cracks in them. Compact shapes have lesser thermal shock resistance properties than porous ones.
VIII. **Mechanical strength-** Cold crushing strength of silica refractories ranges from 250-450 kg/cm2 depending upon the amount and type of bonding agents present and method of production.
IX. **Thermal conductivity-** Thermal conductivity of silica refractories is higher than fireclay refractories. It varies from 0.003-0.004 gm/cal/cm/sec at a temperature of 700.c to 1100.c.

**Applications-** High heat duty silica refractories for their close fitting properties at high temperatures, have found application in open hearth furnace roofs besides arches, crowns and other higher parts of the various furnaces and kilns.

Silica refractories being good heat conductors. They have been used extensively in the construction of coke ovens in numerous shape and size viz. oven walls, jamp blocks, top flue blocks, the sole and roof of ovens etc.

Semi-silica refractories have better spalling resistance than silica refractories but are less refractory. These may be used as backing layers for silica refractories in coke ovens, kiln roof etc. Their properties make them suitable for use in the construction of reheating furnace roofs, regenerator chambers, furnace doors etc.

3 **Dolomite refractories-** Dolomite mineral is a double carbonate of calcium and magnesium having formula CaCO3.MgCo3. Dolomite contains 30.41% CaO, 21.87% MgO and 47.72%CO2.

Dolomites used for the manufacture of refractories should be a mixture of equimolecular properties of CaCO3 and MgCO3 with about 54.35%CaCO3 and 45.65%MgCO3.

Dolomite used should be hard and compact with uniform texture containing very low percentages of iron, silica, alumina, etc. These materials reduce the refractoriness of dolomite refractories.

**Manufacture:-**

1. Stabilization of dolomite- As mined dolomite is dead burnt at 1600.c or more in rotary kilns in presence of serpentine (MgO.2SiO.2H2O). It is added for stabilization of dolomite.

$$CaCO3.MgCO3 \xrightarrow[\text{Serpentine}]{\text{1600. C}} CaCO+MgCO+2CO2$$

After dead burning dolomite contains about 58%CaO and 42%MgO. Dead burnt dolomite undergoes hydration when exposed to atmosphere and hence it is difficult to make refractories from it. To prevent hydration of dolomite refractories they are coated with wax or tar just after firing and cooling.

Furnaces are then constructed from these coated refractories. Once the furnace is put on fire i.e. heated. It is never cooled to the atmospheric temperature. Otherwise their hydration will take place and furnace lining will disintegrate.

Stabilization of dolomite can also be prevented by making dolomite inactive by covering it into a silicate or some other compounds having high fusion temperature. In this case stabilization is achieved by heating dolomite and serpentine ($MgO.2SiO.2H_2O$) in rotary kiln at temperature of 1600.C or more for a period sufficient to ensure completion of conversion reactions. Dolomite and serpentine are mixed in proper portion in ball mill.

2 **Bonding-** In these refractories is achieved by addition of some organic material. For ex: - tar, plastic, lime, magnesium silicate, magnesium chloride, milk of lime, basic slag etc are used as bonding agents.

3 **Mixing-** clinker obtained from the calcinations kiln is cooled, crushed and ground to the desired particle size. The grading of particles is as follows-

| PARTICLE | PERCENTAGE |
|---|---|
| Coarse | 55-57% |
| Medium | 5-15% |
| Fine | 20-40% |

After proper grading, it is mixed with desired amount of bonding material and 4% of water to from semi-dry mass.

4 **Shaping-** The mixture obtain is then moulded into desired shapes by hydraulic pressing under high pressure of about 700 kg/cm2. This produces required strength in moulded shapes.

5 **Drying-** Drying of shaped refractory is carried out with the help of hot dry clean air at a temperature below 60.C. At high temperature cracks will developed in shaped refractories.

6 **Firing-** Firing is carried out in down draught kilns at temperature of 1450.C for 24 hours.

**PROPERTIES-** properties of dolomite refractories very widely depending upon composition and process of manufacture.

1**. Colour-** Color of dolomite refractories varies from white to buff depending upon percentage of iron and other impurities present in them.

2. **Porosity-** Porosity of dolomite refractories is about 23% and have specific gravity of about 3.2.

3. **Refractoriness-** Refractoriness of these refractories varies from 1640.C-2130.C depending upon their composition and structure.

4. **Refractoriness under load-** Refractoriness under load of dolomite refractories containing tri-calcium silicate and Periclase is about 1650.C.

5. **Chemical activity-** Dolomite refractories have good resistance to molten steel but have low resistance to iron oxide and lime slag attack.
6. **Thermal fatigue-** These refractories have low thermal shock resistance as compared to Magnesite refractories. They have good volume stability at 1500.C.
7. **Cold crushing strength-** Cold crushing strength of dolomite refractories is above 400kg/cm2.

**Application:-**
1. Tar dolomite mixture are used as monolithic lining of L.D. and basic Bessemer convertor.
2. These are also used as ramming mixture for basic open-hearth and electric furnaces.
3. Dolomite of 3-10 mesh size are used as fettling material for patch repairs of these furnace after the metal has been taped out while they are still hot.
4. These are also used to close tap holes of basic open hearth furnace.
5. These refractories have better resistance to soda slag than fire bricks so these are used in lining Ladles used for de-suiphurization.
6. Unfired dolomite is used for making upper parts of stopper rods because of their good thermal shock resistance and better resistance to corrosive action of slag than fire clay refractories.

4. **CHROMITE REFRACTORIES-** Chromite is mainly produced in USSR, South Africa, Philippines, and Turkey. In India it is found in Orissa, Karnataka, Tamilnadu, Maharashtra, Bihar and Andhra Pradesh.
**1 Raw materials-** Chromite refractories are produced from chrome ores which is a spinal having the formula FeO.Cr2O3. Chrome ore contain Cr2O3, silica, iron oxide, magnesium like serpentine, chlorite and talc, calcium oxide and alumina as main constituents. Chrome ores used to manufacture chromite refractories contain following composition:-

| Mineral | Percentage |
|---|---|
| 1. $Cr_2O_3$ | 45% |
| 2. Iron oxide | 18%(MAX) |
| 3. Silicate of magnesium | 10-15% |
| 4. CaO | 1.0%(MAX) |
| 5. $SiO_2$ | 3-5% |

| | |
|---|---|
| 6. $Al_2O_3$ | 7-10% |
| 7. $TiO_2$ and alkalis | 1%(MAX) |

$Cr_2O_3$ content of chrome ores varies from 35-55% but chrome ore used to manufacture should have at least 40% $Cr_2O_3$. The percentage of silica and iron should be low as possible as hard and Lumpy and should have fine crystalline structure.

2. **Binder-** Tar is commonly used as bonding material though some other organic substances are also used to bind the ore particles together.

3. **Mixing-** ore is crushed and ground to desired particle size and is then mixed with proper proportions of bond material and water to make plastic paste. Dry mixing is also done. When tar is used as the binding material. It is heated to make it fluid and powdered chrome ore is mixed with it.

4. **Shaping-** Shaping is carried out by hand or by machines.

5. **Drying-** After shaping the refractories are dried slowly to avoid uneven drying and crack formations.

6. **Firing-** Firing is carried out in batch or continuous type kilns, low rate of heating is usually maintained to control swelling. Close packing of these refractories in the kilns is not done because these refractories expend on heating. Maximum temperature is kept 1400.C.

**PROPERTIES-** Properties of Chromite refractories depends upon composition of chrome ore and type of bond material used:-

1 Porosity- Porosity of Chromite refractories is about 24-27%.

2 Special gravity- Specific gravity of chromite refractories varies from 3.8-4.0 depending upon their composition.

3 Refractoriness- Refractoriness of chromite bricks depends upon the percentage of impurities present, mainly silica/silicates and type of bond material used. Refractories made from low silica content have fusion temperature of 1900.C.

4 Refractoriness under load- chromite refractories generally fail at 1400-1450.c under a load of 2kgf/cm2.

5 Thermal fatigue (T.S.R)- Thermal fatigue of Chromite refractories depends upon presence of free silica. It increase with decrease of free silica.

6 Chemical activity- Chromite refractories are resistant to basic slag. These are slightly attacked by acidic slag's.

7 Cold crushing strength- Cold crushing strength of Chromite refractories varies from 350-560kg/cm2.
8 Thermal conductivity - They have low thermal conductivity.

APPLICATIONS:-
1. Chromite refractories are mainly used in non-ferrous and steel industries. These are mainly used for re-heating furnace like bottom of soaking pits used in rolling mills.
2. These are used to separating layers between acid and basic lining in basic open hearth furnace to prevent their chemical action with each other.

5 **MAGNESITE REFRACTORIES:-**
1 **Raw materials-**
**A. Magnesite-** Magnesite refractories are made from naturally occurring magnesium carbonate ($MgCO_3$). These refractories are basic in nature. When it is heated between 400-900.C it ($MgCO_3$) decomposes into magnesia (MgO) and carbon dioxide ($CO_2$). Magnesite should contain good amount (6%) of iron oxide to achieve stability at lower temperature.
**B. Magnisum hydroxide-** Magnesium refractories can also be made from magnesium hydroxide Mg (OH)2. It is made from sea water by its treatment with slaked dolomite.
2 **Preparation of magnesite-**

**1 Preparation of magnesite-** To prepare Magnesite ($MgCO_3$) for manufacture of magnesite refractories. It is dead burnt at 1500-1700.C. By dead burning $CO_2$ will be eliminated and magnesia crystals will formed known as Periclase. These Periclase are stable and undergoes very low shrinkage on when re-burnt.
2 **Preparation of magnesium hydroxide-** Magnesium hydroxide is produced from sea water by its treatment with slaked dolomite. magnesium hydroxide precipitated is filter pressed, then fired in rotary kilns at about 1600-1700.c to form magnesia by following reaction-

$$Mg(OH)_2 \longrightarrow MgO + H_2O$$

3 **Crushing and grinding-** after dead burning of size 110-130mm are obtained which are than crushed and ground to size up to 5mm.

4 **Binding-** After crushing and grinding bounding between burnt magnesite particles is obtained by adding clay, sodium silicate, milk of lime, feldspar, boric acid, caustic soda, Magnesium chloride, magnesium sulphate, iron oxide, tar, gum, dextrin, graphite etc are added depends upon type of raw material used and desired properties required in magnesite refractories.

5 **Mixing-** Finely crushed dead burnt magnesite is mixed with water 4-7% and require amount of bond material to obtained proper plasticity. The dead burnt ground material should have following size-

-1.50mm+0.50mm=45%
-0.50mm+0.125mm=10%
-0.125mm=45%

6 **Moulding-** Shaping of refractories is done generally by hydraulic pressing at about 1000kg/cm2 pressure.

7 **Drying-** After shaping drying is carried out at temperature of 20 to 30.c. Drying take place for 3weeks or more. Refractories having even fine cracks are rejected.

8 **Firing-** Firing is carried out in down draught kilns, chamber kilns or tunnel kilns. Firing temperature is kept 1600-1800.c. for about upto 8hours.

**PROPERATIES-**

1 Color- Magnesite refractories are usually grey to dark brown in color depending on the amount of iron and other ingredients present in them. Refractories free from iron and other impurities are white.

2 Specific gravity- These refractories are dense textures due to high moulding pressure and their specific gravity varies from 3.4-3.6.

3 Porosity- they should have maximum 24% porosity.

4 Refractoriness- A good quality magnesite refractory does not fuse below 2000.C. Impurities like alumina, calcium oxide, silica, alkalies etc reduces the refractoriness of magnesite refractories.

5 Refractoriness under load- refractoriness under load of magnesite refractories varies from 1525-1575.C at a load of 2kgf/cm2.

6 Heat conductivity- Heat conductivity of magnesite refractories decrease with the increase in temperature at 300.C. Their heat conductivity is about 25BTU.

7 Electrical conductivity- These refractories have considerable electrical conductivity at temperature of about 1500.C.
8 Slag attack- Magnesite refractories are basic in nature so higher resistance to the action of basic slag's rich in iron oxide and lime.
9 Thermal fatigue- These refractories have very low resistance to abrasion and sudden change in temperature.
10 Cold crushing strength- Cold crushing strength of pressed magnesite refractories should not be less than 350kg/cm2.

**APPLICATION:-**

1. The use of magnesite refractories is limited for their comparatively low refractoriness under load, low resistance to thermal fatigue, high thermal conductivity and high cost.
2. These are used where slag are basic and there is less changes in temperature. For example-open hearth furnaces, L.D. convertors, electrical are furnace and other steel making furnace.
3. It is used to make socking pits and furnace used for refining metals like Gold, Silver and Platinum.
4. These are used in non-ferrous industries metal like copper, lead, antimony and nickel.
5. Clay bonded magnesite refractories are used to make induction furnace, crucibles used for melting non-ferrous alloys.
6. For repair and construction of open hearth furnace.

6 **Chrome –magnesite refractories-** Chrome-magnesite refractories are made from mixtures of chrome and magnesite ores. Chrome ore ($FeO.C_2O_3$) is present in more quantity and hence are basic in nature.
1 **Preparation of raw material-** Chrome and magnesite ores are prepared separately. Chrome is used in the form of grains are prepared from mined raw chromite which is crushed, ground, sieved and graded. Magnesite ore is first Calcined to form Periclase crystal (magnesia) and then ground.
2 **Mixing-** Ground chromite and Periclase crystals are mixed in a ratio of 70:30 in edge runners or pug mills with proper amounts of bond material. The mixed material must have minimum of 18% chromium oxide and minimum 30% periclase.
3 **Bonding-** Bonding is achieved by adding organic binder to impact mechanical strength.

4 **Shaping-** Shaping of chrome-magnesite is done by hydraulic or mechanical presses under a pressure of 850kgf/cm2.
5 **Drying-** Drying is carried out at temperature of 60-80.c under controlled atmospheric conditions.
6 **Firing-** Firing of chrome-magnesite is carried out in oil or gas fired tunnel kiln at temperature of 1500-1600.C.
7 **Cooling-** After burning these refractories are cooled slowly to avoid disintegration.

**PROPERTIES-**
1 **Colour-** Its colors varies from grey to dark brown depending upon impurities present mostly the percentage of iron.
2 **Specific gravity-** Their specific gravity is about 3.8 so it is 1.5 times heavier than silica refractories (specific gravity 2.3), since these refractories are heavy so, structure of kiln lining must be strong.
3 **Apparent porosity-** Its porosity varies from 22-26%. Denser refractories can be made but porosity is introduced knowingly to avoid failures of roof.
4 **Refractoriness-** Refractoriness of chrome-magnesite refractories is above 2000.C.
5 **Refractoriness under load-** Refractoriness under load of chrome-magnesite refractories is 1600.c. at a load 2kgf/cm2. Refractoriness used for suit roof lining must withstand 1700.c under same load.
6 **Thermal fatigue resistance-** Thermal fatigue resistance of chrome-magnesite refractories is low but higher than magnesite or chromite refractories. It is less then fireclay refractories. It must withstand 20 thermal cycle.
7 **Chemical activity-** These refractories are basic in nature so these refractories resist the action of basic slag.
8 **Cold crushing strength-** Cold crushing strength of chrome-magnesite must be 250kgf/cm2 for burnt quality and 400kgf/cm2 for chemically bonded general purpose refractories. For roof lining it must be 450kgf/cm2 for chemical bonded refractories.

**APPLICATION-**
1. These refractories are mainly used for basic open hearth furnace for various parts like bulk head wall, front and back walls, air and gas bridge wall, air uptakes, slag pocket roof etc.

2. These are also used in side walls of socking pits, copper smelting and copper convertors.
3. These are also used in furnace used for melting, re-melting and refining of aluminum alloys.
4. These refractories are also used for making basic steel making furnace. These are not used for making good quality steel picks up chromium oxide.

7. **Magnesite-chrome refractories-**
1 **Raw material-** The refractories are made from magnesite and chrome ores. The magnesite is major constituent. Both ores are prepared separately and then mixed as per required composition. These refractories must have minimum of 55% periclase (MgO) and 6% chromium oxide (Cr2O3) for general purpose. When refractories are to be used for roof lining there should have 65% Periclase (Magnesia) and minimum 10% chromium oxide.
The silica must not be greater than 5%.
2 **Bonding-** Bonding is achieved by using organic binders, clay or tar.
3 **Raw material preparation-** Chrome ores and magnesite ores are prepared separately. Chrome is used in form of grains. These grains are prepared from mined raw chromite which is crushed, ground, sieved and graded. Magnesite ore is first Calcined to form periclase crystal (Magnesia) and then ground.
4 **Mixing-** Both ores are mixed in required proportion along with binders.
5 **Shaping-** Shaping of magnesite-chrome refractories is done by hydraulic or mechanical presses under a presses under a pressure of 850kgf/cm2.
6 **Drying-** Drying is carried out a temperature of 62-80.C under controlled Atmospheric conditions.
7 **Firing-** Firing is carried out in oil or gas fired tunnel kiln or coal fired batch kiln at temperature of 1500-1600.c.
8 **Cooling-** After burning these refractories area cooled slowly to avoid disintegration.

**PROPERTIES-**

I. Colour- It varies from grey to dark brown depending upon percentage of impurities mainly iron oxide.

II. Apparent porosity- For general purpose used refractories, it should be maximum 24%. For roof lining it should be minimum 23%.
III. Refractoriness- These refractories are do not fuse below 2000.c.
IV. Refractoriness under load- Refractoriness under load of magnesite-chrome refractories is 1550.c at load 2kgf/cm2.
V. Thermal shock resistance- These have better spalling resistance then chrome magnesite and silica, so these are used for roof lining in place of silica refractories in open hearth furnace and other basic furnace. They should withstand minimum 20 thermal cycle.
VI. Cold crushing strength- For general purpose these should be 250-450 kgf/cm2 and for roof lining it should be 450 kgf/cm2.
VII. Chemical activity- These are basic in nature hence resist the action of basic slag.

**APPLICATION-**

1. Due to better spalling resistance, these are used for roof lining in open and other basic furnace. These refractories have increased life of roof lining and working temperature of the furnace.
2. These cannot be used for roof arc due to high thermal co-efficient of expansion.
3. These refractories are mainly used in basic open hearth furnace for making air uptakes, slag pocket roofs, port roofs, gas uptakes, burner zones, back and front walls etc in basic open heath furnace.
4. These refractories have higher resistance to corrosive action of iron oxide and hence these are mainly used electric steel making furnace re-heating furnace and soaking pits.
5. These are also used for lining of reverbratory furnace used for copper smelting and also used for lining cement kilns.
6. These are also used in open induction furnaces used for precision alloys.

8 **Carbon refractories-** Carbon refractories having very high refractoriness, high thermal conductivity and non-wetting characteristics. It is used as

refractory material in construction of furnace used in iron and steel industries. Carbon is found in nature either in amorphous (vitreous) or crystalline form.

1. Raw material- Carbon refractories are manufactured from coke or graphite. The graphite structure is hexagonal frame work. The natural graphic occur in different types of ore deposits-

1. Crystalline flake graphite (flake graphite).

2. Amorphous graphite.

3. Lump graphite.

**Composition of graphite-** Graphite contains about 7.5 to 12.5% ash. The ash analysis of graphic contains 42-54% $SiO_2$,15-50% $Al_2O_3$,0.9-1.4% $TiO_2$,13-28% $Fe_2O_3$,1-4.5%CaO,3.5-8.5%MgO,2.2-2.6%$K_2O$,0.1-2.5%$Na_2O$.

2. **Raw material preparation-** Coke containing as little as possible of ash (about8%) is crushed and ground to a particle size of 1-2mm and kept in a dry place. Bond used is tar, pitch, fireclay, milk of lime, sodium silicate etc.

After grinding 7-10kg of coke powder is spread on clean floor and hot tar or pitch is poured on it, then it is mixed with the help of shovels. Mixing in large quantities is not carried out as tar will cool before mixing and will gives rise to the formation of balls.

3. **Moulding-** The shaping is carried out in wooden or iron moulds. Hot tarred mixed material are placed on base of mould. Moulds and base Boards are oiled before use. The material is rammed by a hot rod of iron or stamps. After ramming excess material is removed and it is allowed to cool. After cooling mould is removed and refractory shapes are obtained. Moulding can also be done by machine pressing when large quantities are required.

4. **Drying-** Drying of moulded shapes is carried out in ventilated rooms without direct sunshine to increase their green strength.

5. **Firing-** Firing of carbon refractories is done/carried out in down draught kiln in absence of air. Shaped refractories are packed with sand and cokes in kiln to prevent distortion during initial heating. After placing the shapes, kiln is made air tight.

Heating is done indirectly. The temperature is increased slowly to 250.C at which tar is converted into coke and refractories gets harden. After that kiln is hearted to about 1300.c to develop high strength. The refractories are kept 50-70 hours at maximum temperature.

After this kiln is cooled very slowly. The kiln are opened and unloaded only when they are cooled at room temperature.

Otherwise refractories may catch fire. The total time of refractories in the kiln is about 200-250 hours.

**PROPERTIES-**

I. Colour- they are light grey in colour and give a ringing sound when struck.
II. Porosity- The porosity of carbon refractory is about 20-25%.
III. Specific gravity- Their specific gravity varies from 1.5-1.9.
IV. Refractoriness- These are solid above 3000.c and if made properly these can attain any temperature.
V. Refractoriness under load- Refractoriness under load of carbon refractories is 1750.c at load 2kgf/cm2.
VI. Chemical activity- Carbon refractories oxidized and burn when exposed to air on heating. They are not attacked by slag because these are non-wetted by melts.
VII. Thermal fatigue resistance- They have a high resistance to fluctuations in temperature which results in high thermal shock resistance.
VIII. Cold crushing strength- Cold crushing strength of carbon refractories is 350kgf/cm2.
IX. Thermal and electrical conductivities- Thermal and electrical conductivities of carbon refractories are very high.

**APPLICATION-**

1. Carbon refractories are mainly used in form of blocks in blast furnace because these can withstand at high temperature, load and chemical actions. Now a days it is used as standard material for lining iron and slag runners. Due to high thermal conductivity these helps in easy control of temperature in lower parts.
2. Carbon as ramming mixtures with tar is used for construction of electrolytic cells. For example- Aluminum reduction cell.
3. Graphite refractories made from fireclay are used as stoppers, nozzles and ladle bricks where slag attack is more.
4. Graphite crucibles are mainly used for melting cast iron, copper, brass, bronze and aluminum.

**8High alumina refractories-** High alumina refractories can be Kyanite, sillimanite, bauxite, mullite or corundum (a alumina) base. High alumina refractories performed better under sever condition then fire clay refractories because of their good volume stability, high resistance to abrasion and erosion, high resistance to thermal shock and creep, high refractoriness, greater load bearing capacity and resistance to slag attack and high cold crushing strength.

**1 Raw materials-** These refractories are made from raw material like bauxite, bauxite clays, Kyanite, andalusite and even chemically produced alumina are used for the manufacture of high alumina refractories. The alumina content can vary from 45-95%.

**2 Bonding-** These refractories may be chemically bonded or ceramic bonded.

**3 Shaping-** These refractories are generally made by dry pressing and some special shapes are made by pneumatic ramming and hand moulding. The raw materials are mostly precalcined in order to give lower firing shrinkage.

**4 Drying-** These refractories are dried slowly to prevent cracks.

**5 Firing-** Firing of high alumina refractories is carried at around 1300-1700.c.

**PROPERTIES-**

1. **Refractoriness-** refractoriness of high alumina refractories is 1800-1850.c.
2. **Apparent porosity-** Apparent porosity of high alumina refractories is 15-25%.
3. **Cold crushing strength-** Cold crushing strength of high alumina refractories is 250-800.
4. **Thermal shock resistance-** Excellent.

**APPLICATION-**

1. High alumina refractories are mainly used in blast furnace stoves and other regenerative furnace, electro are furnace roofs, rotary kilns, ladles, cement and lime kilns, glass melting furnace etc.

2. Chemically bonded high alumina refractories are mainly used for alumina melting and holding furnace due to their non-wetting characteristics.

10 **Electro-cast or Fusion cast refractories**

These refractories are manufactures by fusing required mixtures of raw materials in electric arc furnace and casting the hot fused mass into special moulds of the desired shapes and size. After this annealing of casted shape is done for better and uniform properties in the casted refractory shapes.

**Raw material-** Alumina, Alumina-silica, Alumina-zirconia, Chrome-alumina etc.

1. **Fused mullite refractories-** These are produced from pure silica and pure alumina. These refractories are better than other alumino-sillcate refractories because complete mullite formation occurs due to fusion.

**PROPERTIES-**

1. These refractory retain their and strength upto1800.c.
2. These are highly resistance to thermal shock resistance.
3. These refractories are highly resistance to attack of molten metal and slags due to neutral character.

**Uses-**

1. These are used in lining ladles, which are used for high temperature steel making.

2. These are also used in re-heating furnace hearths, cupola slag pocket arches, heat treatment and re-heating furnace which are subjected to thermal shocks.

2. **Fused Alumina refractory-** These refractories are produced by fusing Bayer quality alumina (99%pure) at above 2000.c by fusing high quality bauxite gives slightly pure brown alumina product.

**PROPERTIES-**

1. Colour- Pure brown colour.
2. Chemical reactivity- These are highly stable to oxidizing or reducing condition.
3. High refractoriness.
4. High ho t strength.
5. High abrasion resistance.

**Uses-**

These are used for lining carbon black reactors, domes of chemical reactors in fertilizer plants, reactor in gasification of petroleum feed stock, catalytic cracking in refineries etc. These are also used in rotary kiln, blast furnace stacks, LD convertors etc.

## Flow chart for manufacturing of refractory

Raw material (Silica, Alumina, Iron oxide, Calcium oxide)

↓

Crushing (Jaw crusher, Hammer mill)

↓

Grinding (Ball mill, Tube mill)

↓

Mixing (Blunger)

↓

Shaping (Hydraulic press, Iso-static press)

↓

Drying (Tunnel dryer)

↓

Firing (Shuttle kiln, Tunnel kiln)

↓

Cooling (Tunnel kiln, Shuttle kiln)

Inspection (Sorting department)

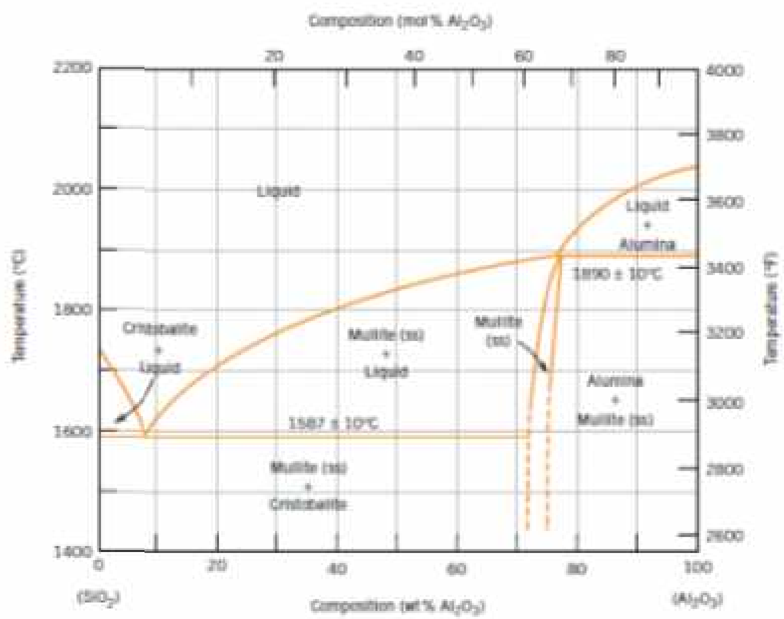
Dispatch

Market

# UNIT IV

# SiO2-Al2O3 phase diagram

**Figure 12.25** The silica-alumina phase diagram; ss denotes solid solution. (Adapted from F. J. Klug, S. Prochazka, and R. H. Doremus, "Alumina-Silica Phase Diagram in the Mullite Region," *J. Am. Ceram. Soc.*, **70**[10], 758 (1987). Reprinted by permission of the American Ceramic Society.)




Mullite melts congruently at 1850°C. The extent of equilibrium solid solution in mullite at solidus temperature is from approximately 60 mole % $Al_2O_3$ (3/2 ratio) to 63 mole % $A1_2O_3$. Metastable solid solutions can be prepared up to about 67 mole % $Al_2O_3$. There is no evidence for stable solubility of excess $SiO_2$ beyond the 3/2 composition at pressures below 3 kbars. Refractive indices are presented for glasses containing up to 60 mole % $Al_2O_3$ and from them the composition of the eutectic is confirmed at 5 mole % $SiO_2$. The variation in lattice constants of the mullite solid solution is not an unequivocal guide to composition since mullite at one composition produced at different temperatures show differences in spacing, no doubt reflecting Al-Si ordering phenomena. The possibility of quartz and corundum being the stable assemblage at some low temperatures and pressures cannot be ruled out. A new anhydrous phase in the system is described, which was previously thought to be synthetic andalusite; it is probably a new polymorph of the $Al_2SiO_5$ composition with ortho-rhombic unit-cell dimensions *a*=7.55 A, *b*=8.27 A, and *c*= 5.66 A.

PHASE DIAGRAM OF $MgO\text{-}SiO_2$