Properties of Refractories

1. Refractoriness

Ability of a material to withstand the heat, without appreciable deformation or softening under particular service conditions.

In general, measured as the softening or melting temperature of the material.

As most of the common refractory materials are mixtures of metallic oxides, so they do not have a sharp fusion temperature.

Pyrometric Cones Test (Segar Cones Test)

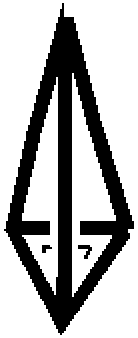
The softening temperature of the refractory material are, generally, determined by using Pyrometric cones test.

Expressed in terms of Pyrometric cone Equivalents (PCE).

Softening temperature (Material to be used as refractory) >> **Operating temperature**

Pyrometric Cones Test (Segar Cones Test)

The refractoriness is, usually, determined by comparing the behaviour of heat on cone of material to be tested with that of a series of Segar cones of standard dimensions.



Segar Cone

Pyramid Shaped having triangular base 38 mm high and 19 mm long sides

Segar cones melt or fuse at definite temperature when heated under standard conditions of 10°C / min.

So the temp. at which the fusion or softening of the test cones occurs is indicated by its apex touching the base.

The PCE value of the given refractory is taken as the no. of the standard cone, which fuses along with the test cone.

Seger cone and reference temperature

Seger Cone No. according to ISO [1]		Melting temp. °C	Seger Cone No. according to ISO [1]		Melting temp. °C
17	150	1500	32.5	172	1720
18	152	1520	33.5	174	1740
19	154	1540	34	176	1760
20	156	1560	35	178	1780
26	158	1580	36	180	1800
27	160	1600	37	183	1830
27.5	162	1620	38	186	1860
28	164	1640	39	188	1880
29	166	1660	40	190	1900
30	168	1680	41	194	1940
31	170	1700	42	198	1980

[1] Small Seger cone, Temperature increase 2.5 °C/min. = 150 °C/h

Segar Cones Number	Fusion temperature
1	1110
2	1120
3	1140
4	1160
5	1180
6	1200
7	1230
8	1250
9	1280

2. Strength or Refractories-under load (RUL):

Refractories used in industrial furnaces have invariably to withstand varying loads of the products, being manufactured at high operating temperature.

It is, therefore, essential that refractory materials must also possess high mechanical strength, even at operating temperature, to bear the maximum possible load, without breaking.

Some refractories like FIRECLAY, High Alumina Bricks softens gradually over the range of temperature, but under appreciable load, they collapse, far below their true fusion point, as determined by segar cones.

On the other hand, other refractories such as Silica Bricks softens over a relatively narrow range of temperature and exerts good load bearing characteristics close to their fusion points.

R.U.L. Test

Refractories-under load Test

R.U.L. test is performed by applying a constant load of 3.5 or 1.75 kg/cm^2 to the refractory specimen (of size 5 cm^2 and 75 cm high) and heating in a carbon-resistance furnaces at a standard rate of 10°C / min.

The record of the height of the specimen vs. temperature is made by a plot, until the test-piece deforms or collapses by 10%.

The R.U.L. is expressed as the temperature at which 10% deformation takes place.

This is a measure of the resistance of a refractory body to the combined effects of heats of load. This test helps to study the behavior of a refractory product when subjected to a constant load under conditions of progressively rising temperature.

Determination of refractoriness under load (RUL)

Characteristic temperatures are	Brick grade	t_a / °c
t_a : 0.3 mm compression from the temperature the temperature of highest expansion (0.6 % compression of test sample)	Fire clay	1300 -1550
	Corundum	1600 - 1750
	Silica	> 1660
	Magnesia chromite	> 1550
t_e : 10 mm compression from the temperature of highest expansion (20 % compression of test sample)	Magnesia-hercynite	1600
	Dolomite	1700
	Magnesia spinel	> 1700
t_b : temperature of breaking sample.	Carbon brick	non-softening

3. Dimensional Stability

Resistance of a material to any volume changes, which may occur on its exposure to high temperature, over a prolonged time.

These dimensional changes may be permanent (irreversible) or reversible.

Irreversible changes may result either in the contraction or expansion of a refractory.

The permanent contraction is due to the formation of increasing amounts of liquid from the low fusible constituents of the refractory brick, when it is subjected to a long period of soaking at the high temperature.

The liquid gradually fills the pores of the refractory body, causing a high degree of vitrification and shrinkage.

4. Chemical Inertness

A refractory should be selected that is chemically inert in use and does not form fusible products with slags, fuel ashes, furnace gases, etc.
usually, the environment in most furnaces are either acidic or basic.

It is not recommended to employ Acid refractory in contact with an alkaline (basic) product or vice-versa.

5. Thermal Expansion

Solid materials, on heating, expands and on cooling it contracts.
So in the designing of the practical furnaces, a refractory material should have least possible thermal expansion as the expansion affects all dimensions (e.g. length, area, volume) of the body.

6. Thermal Conductivity

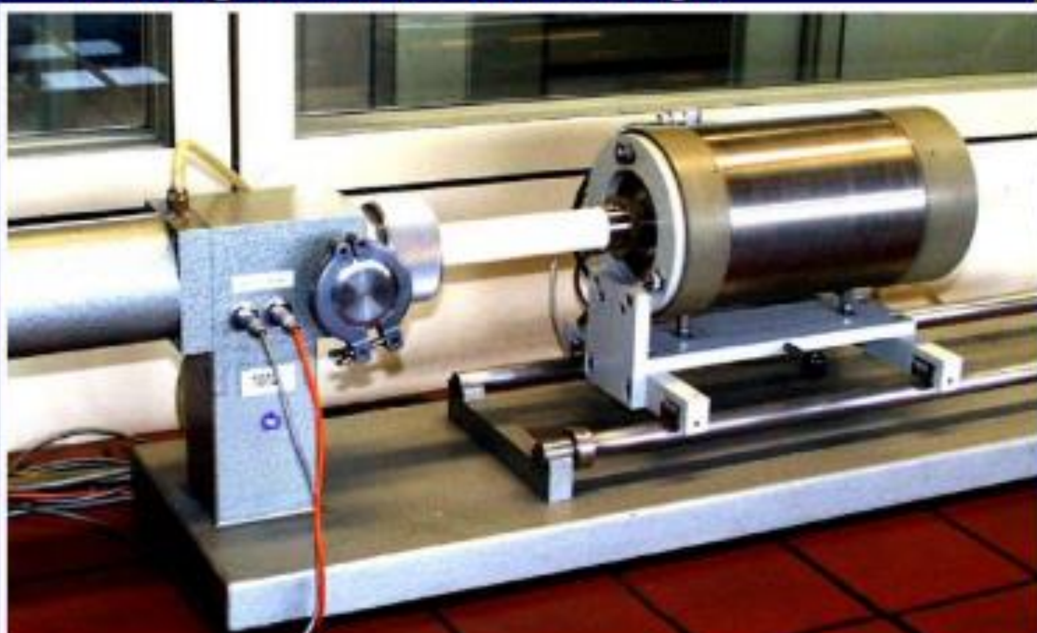
In industrial operations, refractory materials of both high thermal conductivity and low thermal conductivity are required, depending upon the type of the furnaces.
In most cases, furnaces is lined with refractories of low heat conductivities to reduce the heat losses to the outside by radiation; otherwise maintenance of high temp. inside furnaces will become difficult.

Linear expansion (Permanent linear change)

High temperature reheat test may be used to reveal

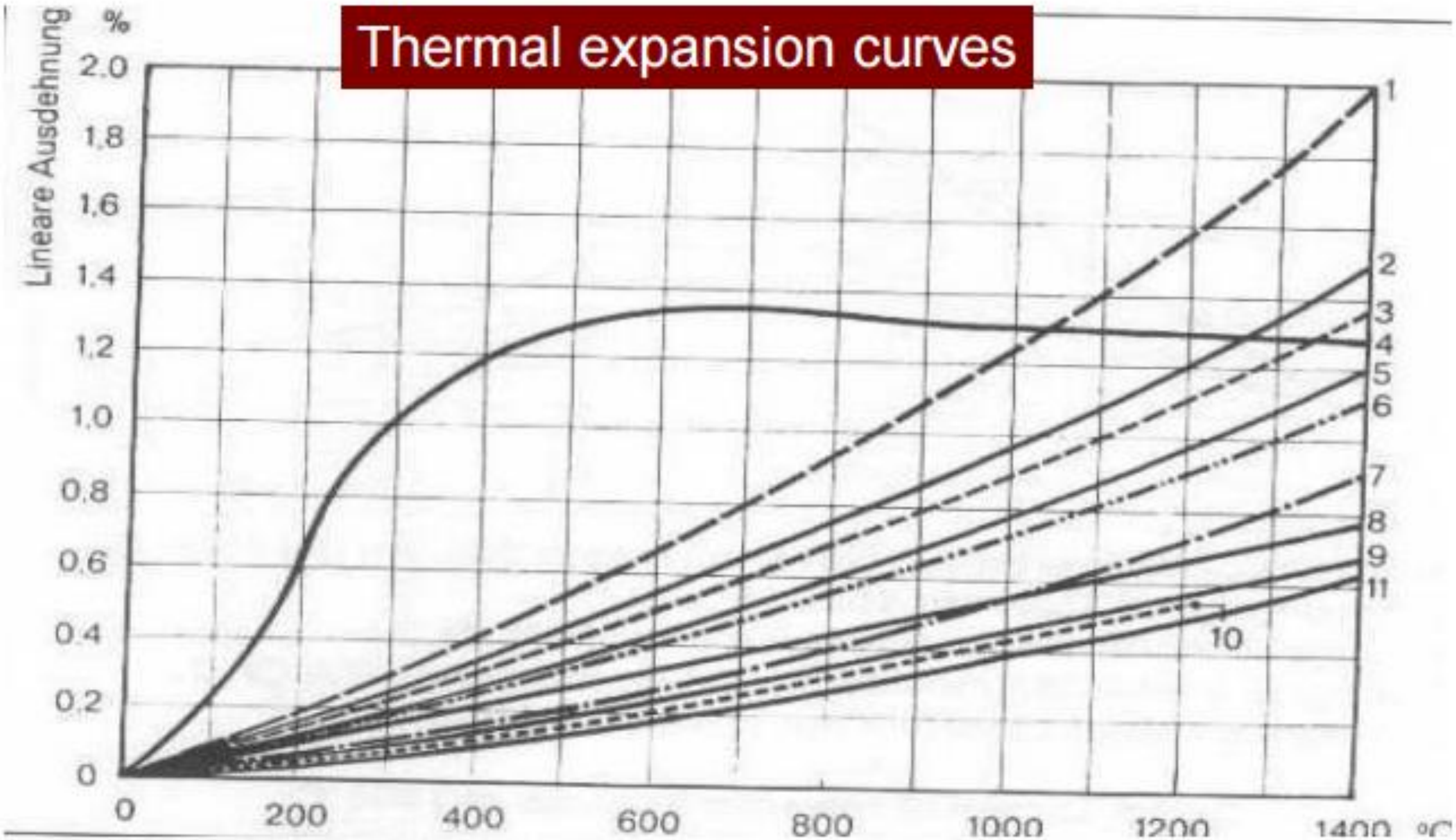
1) if a brick has been fired long enough or at a high temperature
2) whether a brick has adequate refractoriness and volume stability

It is expressed as a percentage , preferably by the ratio of the length of the test piece after heating and the original value of the length



Equipments used to determine Thermal expansion

Thermal expansion curves



Picture 63: Thermal expansion of refractory bricks:
1.Magnesia • 2. Chrome-Magnesia • 3. Chromite • 4. Silica
5. Zirconia • 6. Corundum 99% • 7. Corundum 90% • 8. Fireclay
9. Sillimanite • 10. Zircon • 11. Silicon Carbide.

Thermal Conductivity

A good heat conductivity of the refractory material is desirable for effective heat transmission in furnace construction.

The densest and least porous brick have the highest thermal conductivity, owing to the absence of air-voids.

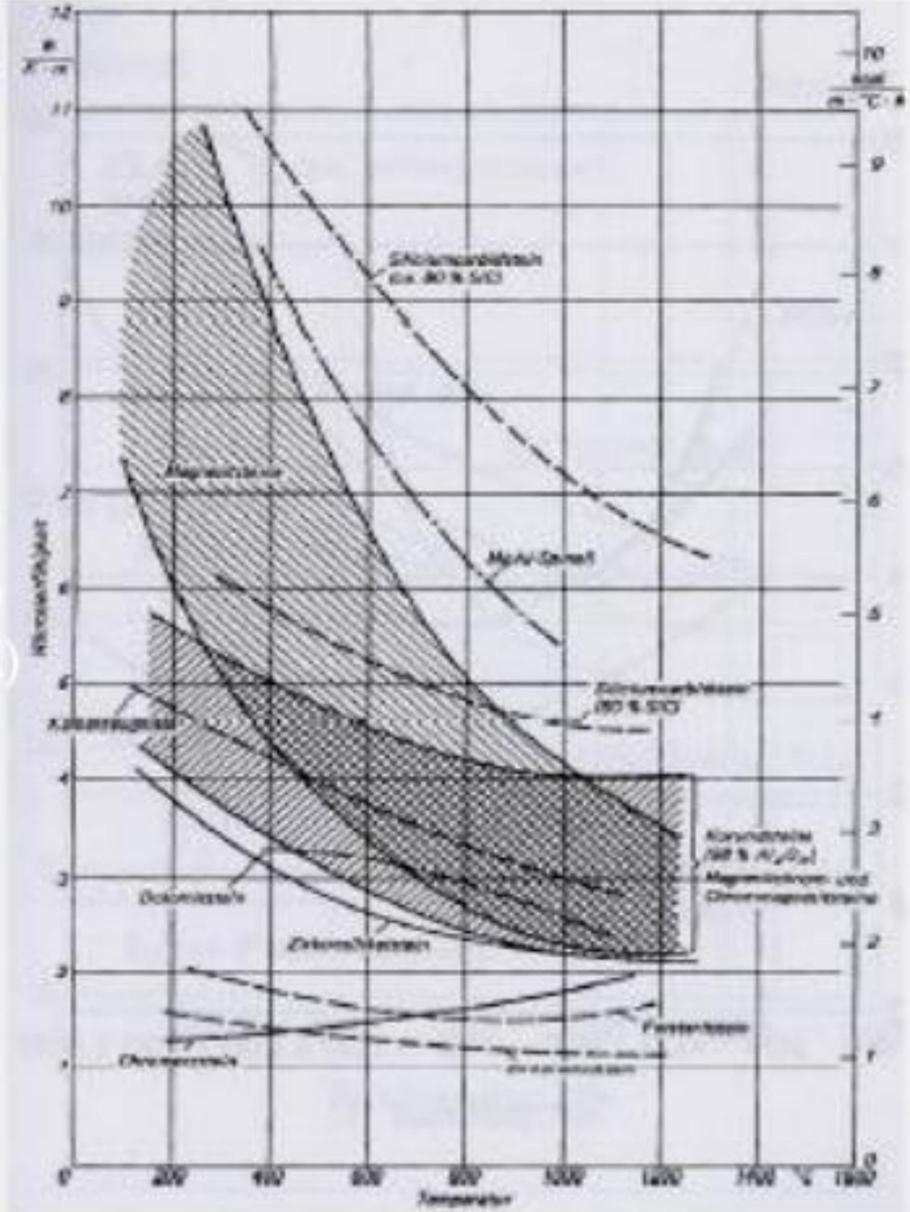
On the other hand, in porous bricks, the entrapped air in the pores, acts as a non-heat conducting material.

For making porous refractory bricks, the refractory material is mixed with a liberal amount of carbonaceous material, then mould into bricks and burnt. The carbonaceous material burns off; leaving behind minute voids, which enhances the insulating quality.

Thermal conductivity

Thermal conductivity depends on temperature , chemical and mineralogical, composition of the brick , porosity, pore size and brick firing temperature

Material	Thermal conductivity at 1000 ^{O} C (W/(m.K))
Magnesia	4.4
Magnesia chromite	2.5
Magnesia –spinel	2.8
Magnesia hercynite	2.6
Alumina	3.0
Insulating brick	0.6
Iron	28.0



7. Porosity

All refractories contain pores, either due to manufacturing methods or deliberately made (by incorporating saw-dust or cork during manufacture).

Porosity is the ratio of its pore's volume to the bulk volume.

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

W = Wt. of saturated specimen.
D = Wt. of Dry specimen.
A = Wt. of saturated specimen submerged in water.

Porosity is an important property of refractory bricks, because it affects many other characteristics, e.g. chemical stability, strength, abrasion-resistance and thermal conductivity.

In a porous refractory, molten charge, slags, gases etc. are likely to enter more easily to a greater depth and may react and reduces the life of the refractory material.

Porosity decreases Strength
resistance to abrasion
resistance to corrosion/ penetration by slags, gases ec.

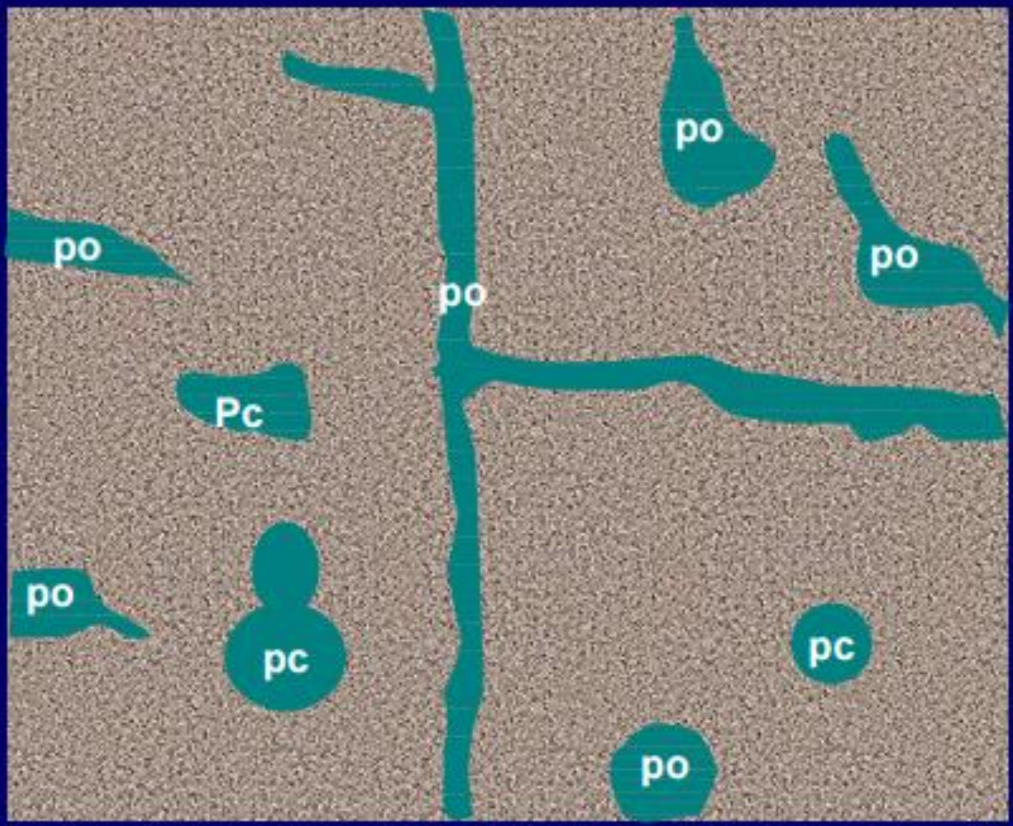
Porosity increases resistance to thermal spalling (i.e. thermal shock-resistance

The densest and least porous brick have the highest thermal conductivity, owing to the absence of air-voids. In porous bricks, the entrapped air in the pores, acts as a non-heat conducting material.

Porosity affects

- the strength of the brick
- porous bricks are mechanically weak
- lower porosity gives better resistance to slag attack
- thermal conductivity

Po –open pores
Pc –closed pores



8. Thermal Spalling

Breaking, cracking, peeling off or fracturing of a refractory brick or block, under high temperature. So good refractory must show a good resistance to thermal spalling.

Spalling is caused by rapid changes in temperature, which causes uneven expansion and contraction within the mass of refractory, thereby leading to development of internal stresses and strains.

Spalling may also be due to slag penetration into the refractory brick, thereby causing variation in the coefficient of expansion.

Spalling can be decreased by

- Using high porosity, low coefficient of expansion and good thermal conductivity refractory bricks.
- Avoiding sudden temp. changes.

9. Resistance to abrasion or erosion

good refractory must show a good resistance to abrasion or erosion.

10. Electrical conductivity

good refractory must show a low electrical conductivity. Except graphite, all other refractories are poor conductors of electricity.

11. Heat capacity

Heat capacity of any substance depends on

(a) Thermal conductivity
(b) Specific heat
(c) Specific gravity

Permeability

Measure of rate of diffusion of gases, liquids and molten solids through a refractory.
Permeability depends upon the size and number of connected pores.

$$\text{Permeability @ temperature} \propto \frac{1}{\text{Viscosity of molten material}}$$

Cold crushing strength (CCS)

Cold crushing strength of a refractory material represents its strength .In other words it tells us how much load it can bear in cold condition

The mechanical strength (CCS) of refractory brick is governed largely by the amount and the character of the matrix material. It indicates the ability of the brick to withstand abrasion and impact in low temperature application.

CCS testing machine

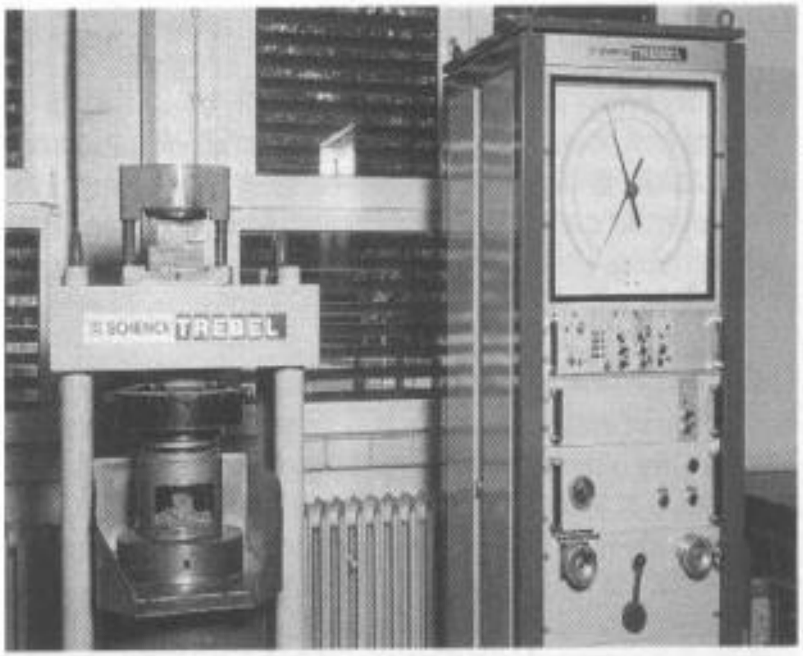


Bild 66a: Prüfapparaturen zur Bestimmung der Kaltdruckfestigkeit.

Picture 66a: Testing apparatus to check cold crushing strength.

Bild 66b: Der Prüfzylinder.

Picture 66b: The test cylinder.

Bild 66c: Probekörper nach Testende

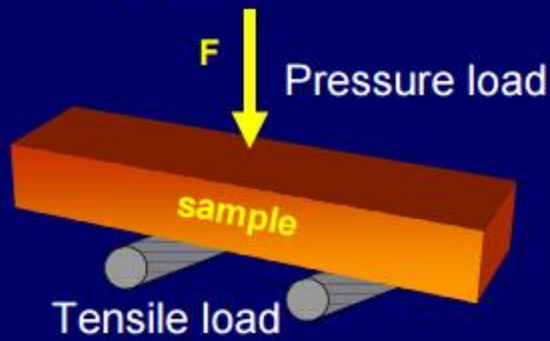
Picture 66c: Specimen after end of test.

Cold crushing equipment and CCS values

Brick grade	CCS (N / mm2
Silica	15 -20
Fire clay	12 - 70
Corundum	35 - 80
Magnesia	50 - 110
Magnesia chromite	30 - 70
Magnesia spinel	> 40
Insulating Brick	3 - 20

Determination of modulus of rupture

In order to determine the magnitude of the rupture stress of refractoies , the resistance to deformation under bending load is measured.



The bending strength can be calculated by means of the equation

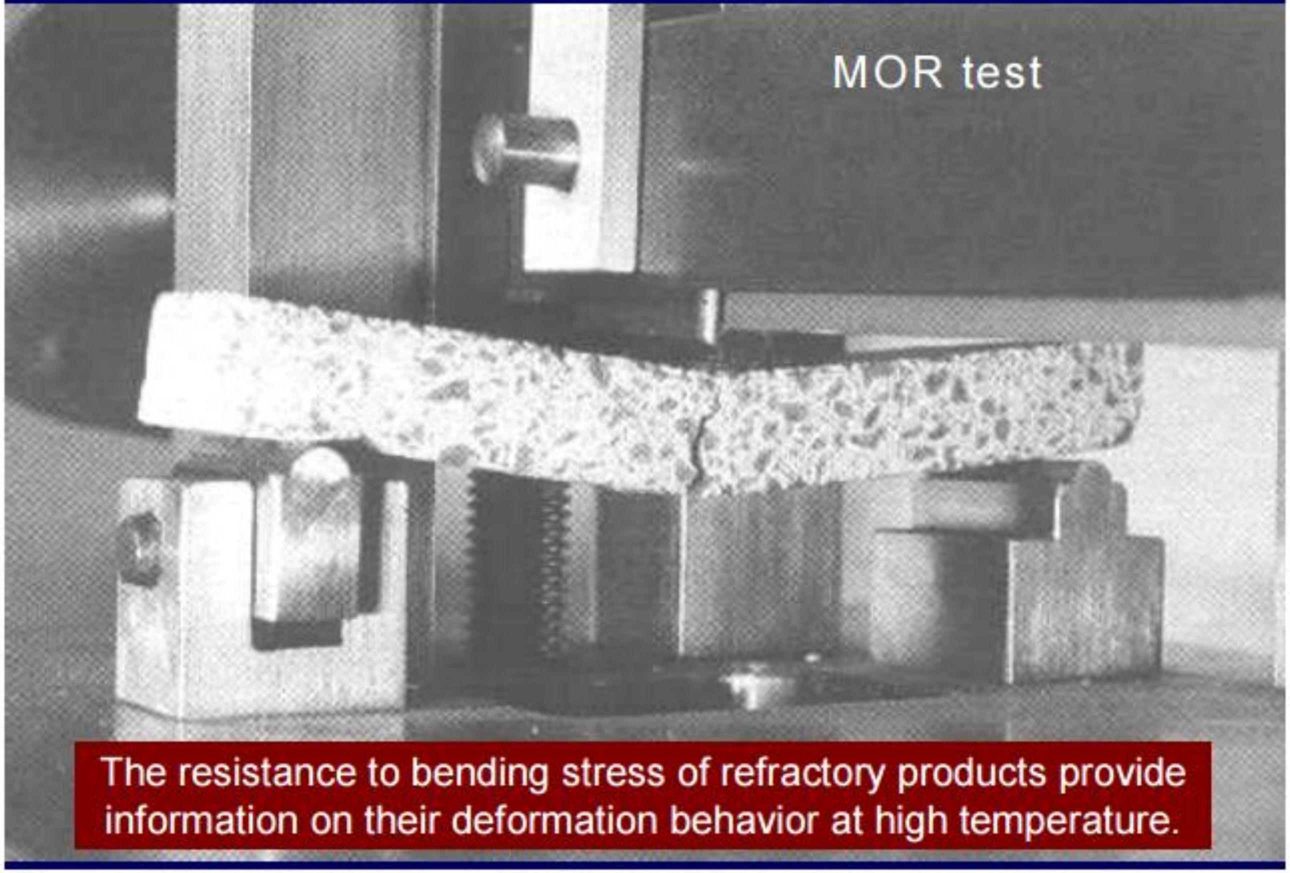
σ bending = 3.F.l / (2.b.h^2)

l = distance between blades

b = width of sample

h= height of sample

Modulus of rupture



The resistance to bending stress of refractory products provide information on their deformation behavior at high temperature.

Cup corrosion test

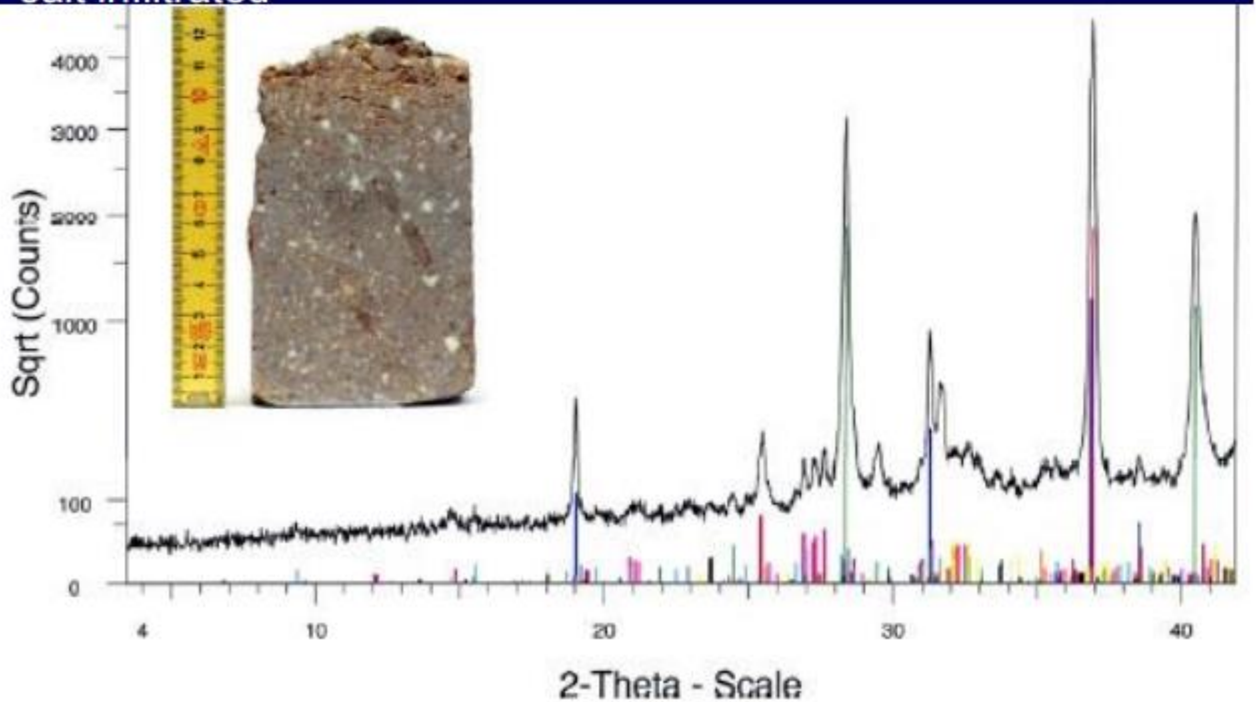
Alkali test of a high alumina brick with K_2CO_3

Alkali test of a sic containing high alumina brick with K_2CO_3

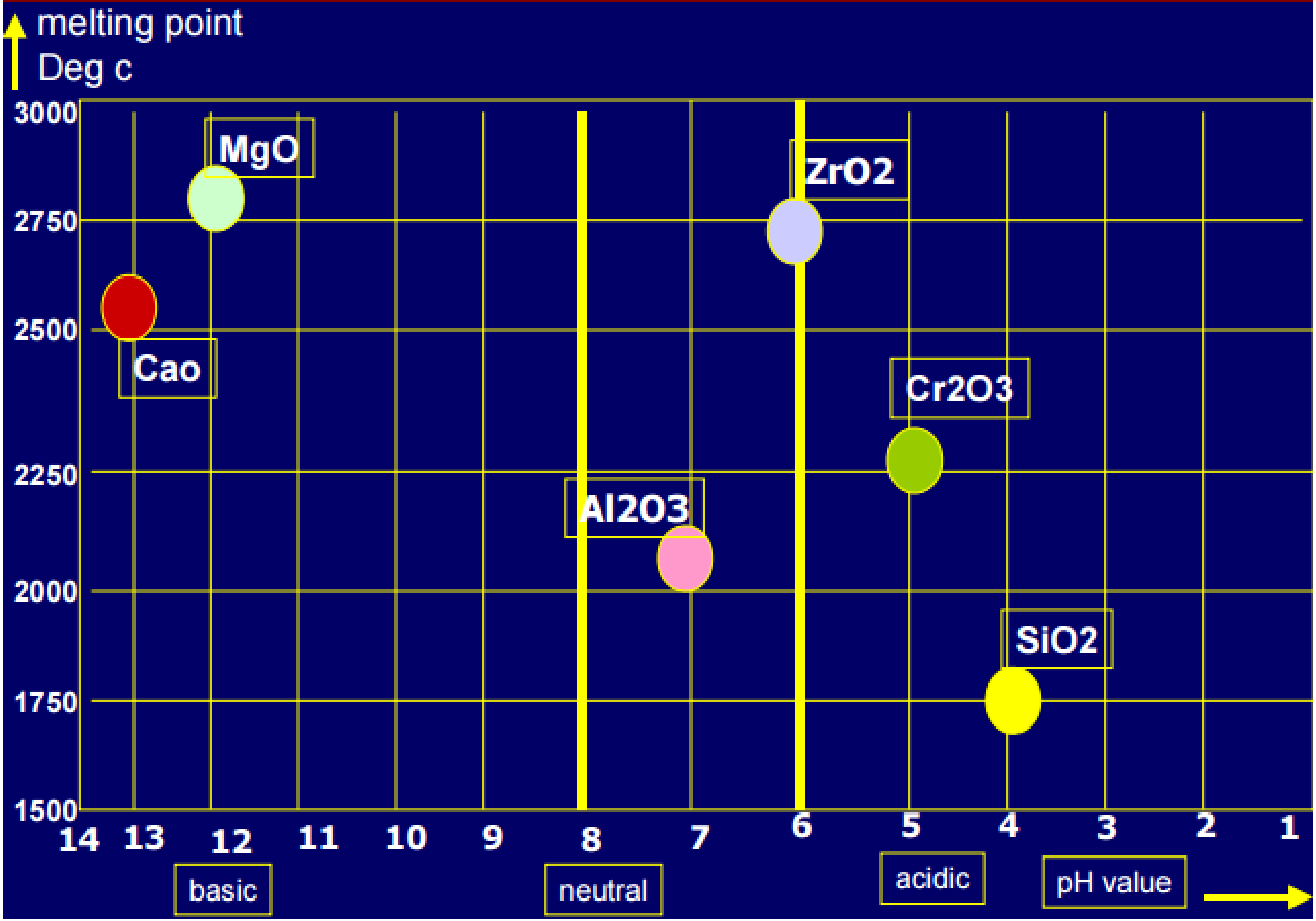
Mineralogical investigations by X-ray diffraction

Determination of the mineral phases composition of material

X-ray diffraction diagram of a used magnesia –spinel brick grade salt infiltrated



Classification of refractories regarding melting point and alkalinity



Classification Based on Physical Form

Refractories are classified according to their physical form. These are the *shaped* and *unshaped* refractories. The *shaped* is commonly known as refractory bricks and the *unshaped* as "monolithic" refractories.

Shaped Refractories:

Shaped refractories are those which have fixed shaped when delivered to the user. These are what we call bricks. Brick shapes maybe divided into two: standard shapes and special shapes.

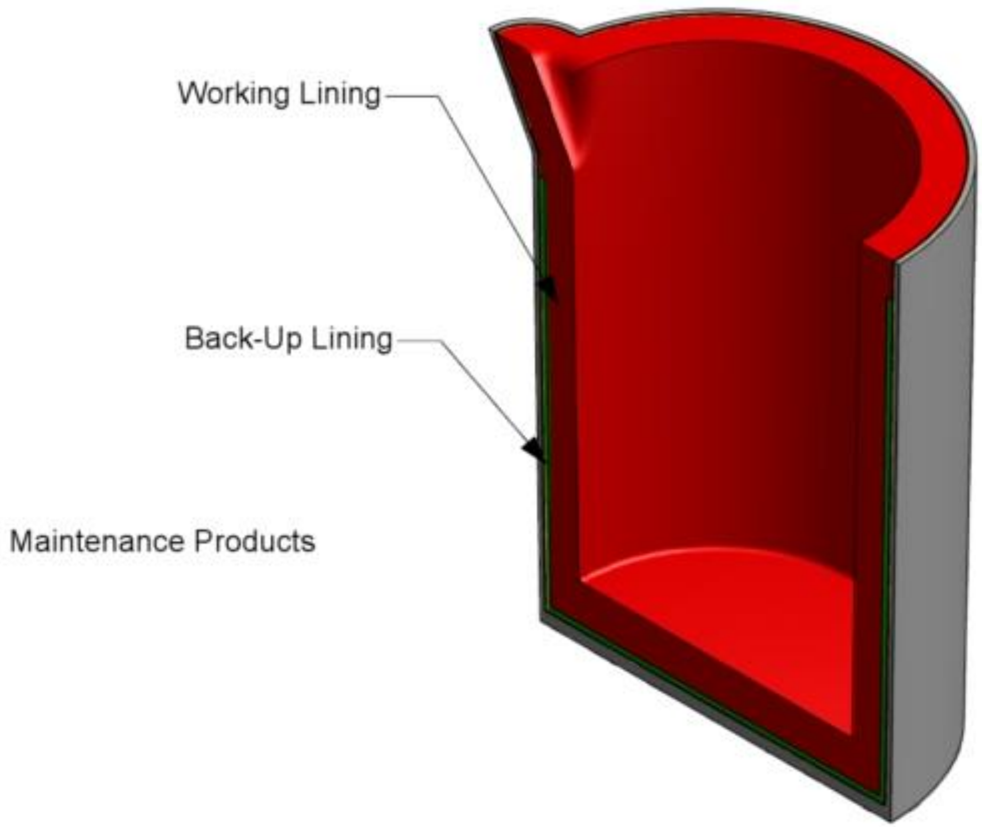
Standards shapes have dimension that are conformed to by most refractory manufacturers and are generally applicable to kilns and furnaces of the same type.

Special shapes are specifically made for particular kilns and furnaces. This may not be applicable to another furnaces or kiln of the same type. Shaped refractories are almost always machine-pressed, thus, high uniformity in properties are expected. Special shapes are most often hand-molded and are expected to exhibit slight variations in properties.

Unshaped Refractories:
Unshaped refractories are without definite form and are only given shape upon application. It forms jointless lining and are better known as **monolithic** refractories. These are categorized as Plastic refractories, ramming mixes, castables, gunning mixes, fettling mixes and mortars.

Plastic refractories are tempered with water and/or added with a binder. They have sufficient plasticity to be pounded or rammed into place

Mouldable mixes are refractories which are installed by hammering or ramming and have sufficient plasticity to mould to whatever shape is required. Ramming mixes usually contain a plastic clay which is tempered with water, de-aired and extruded into blocks


Working Lining
Back-Up Lining
Maintenance Products

Classification Based on The Refractoriness

S.NO	TYPE OF REFRACTORIES	PCE VALUE	REFRACTORINESS(^{0}C)	EXAMPLES
1	Low heat duty refractories	19-28	1520 – 1630	Silica bricks
2	Intermediate heat duty refractories	28-30	1630 – 1670	Fireclay bricks
3	High heat duty refractories	30-33	1670 – 1730	Chromite bricks
4	Super heat duty refractories	>33	>1730	Magnesite bricks

Types of Refractories

Refractories are classified as dense or insulating types.

- The most high-temperature refractories, such as firebricks, are high-density (>1,92 gr/cm^3). They offer excellent resistance in challenging operating environments, such as slags with different chemical compositions, fumes, dust, and gases.

- Insulating refractories have lower densities (0,06 to 1,12 gr/cm^3) and provide insulating properties, while offering resistance to corrosion and chemical reactions with the operating environment.

The following is the discussion of the outstanding characteristics of the various types of refractories :

1) Fire-clay Brick Refractories

- Fire-clay brick comprise about 75% of the production of refractories on a volume basis and are essentially hydrated aluminum silicates with minor proportions of other minerals.

- Typical composition consists of SiO_2<78% and Al_2O_3< 44%.

- As a type they are extremely versatile; least costly of all refractory bricks and are extensively used in the iron and steel industry, non ferrous metallurgy, glass industry, pottery kilns, cement industry and by many others.

- All fire-clay brick are not alike and the total ranges of their properties are quite broad.

- ASTM subdivides fire-clay brick into four major classifications depending primarily upon fusion temperature (Pyrometric Cone Equivalent, PCE).

- The four standard classes of fireclay brick are: super duty, high-duty, medium-duty, low-duty, and also semi-silica.
- These classes cover the range from approximately 18% to 44% alumina, and from about 50% to 80% silica.
- Table below shows that as the quantity of impurities increases and the amount of Al_2O_3 decreases, the melting point of fireclay brick decreases.

Brick	% SiO_2	% Al_2O_3	Other Constituents	PCE °F
Super Duty	49-53	40-44	5-7	3175-3200
High Duty	50-80	35-40	5-9	3075-3175
Medium Duty	60-70	26-36	5-9	2975-3075
Low Duty	60-70	23-33	6-10	2770-2900

-32 x 5/9 → 932 F = 500 C

- Characteristically, fire-clay brick begin to soften far below their fusion temperature and under load actual deformation takes place.
- The amount of deformation depends upon the load, and, once started, this deformation is a slow but continuous process unless either the load or the temperature is reduced.
- It is for this reason that fire-clay brick are not well adapted for use in wide sprung arches in furnaces operating continuously at high temperatures.

2) High Alumina Refractories

- Alumina refractory which consists of aluminum oxide and traces of other materials is the most mature of the engineering ceramics.
- Alumina is one of the most chemically stable oxides known, which offers excellent hardness, strength and spallingresistance.
- It is insoluble in water and super heated steam, and in most inorganic acids and alkalis.
- Alumina refractories carry the all purpose characteristics of fire-clay brick into higher temperature ranges that makes it suitable for lining furnace operating up to 3350°F.
- It has a high resistance in oxidizing and reducing atmosphere and is extensively used in heat processing industries.
- The refractoriness of high alumina refractories increases with increase of alumina percentage.
- The 50%, 60%, 70% and 80% alumina classes contain their respective alumina contents with an allowable range of plus or minus 2.5%.
- High-alumina brick are classified by their alumina content according to the following ASTM convention. These are:

Mullite refractory: Mullite brick is about 72wt% alumina with 28wt% silica. These have excellent volume stability and strength at high temperatures.

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

High alumina bricks are most commonly used in cement, lime and ceramic kilns, glass tanks, crucibles for melting a wide range of metals, hearth & shaft of blast furnaces and in lead drossing furnaces.

3) Silica Brick

Silica brick is a refractory that contains at least 93 percent SiO_2. The raw material is high quality rocks. Various grades of silica brick have found extensive use in the iron and steel melting furnaces and the glass industry. In addition to high fusion point multi-type refractories, other important properties are their high resistance to thermal shock and their high refractoriness. The outstanding property of silica brick is that it does not begin to soften under high loads until its fusion point is approached. This behavior contrasts with that of many other refractories, for example alumina silicate materials, which begin to fuse and creep at temperatures considerably lower than their fusion points. Other advantages are flux and stag resistance, volume stability and high spalling resistance.

4) Magnesite Brick

Magnesite refractories are chemically basic materials, containing at least 85 percent magnesium oxide. They are made from naturally occurring magnesite ($MgCO_3$). The properties of magnesite refractories depend on the concentration of silicate bond at the operating temperatures. Good quality magnesite usually results from a CaO-SiO_2 ratio of less than two with a minimum ferrite concentration, particularly if the furnaces lined with the refractory operate in oxidizing and reducing conditions. The slag resistance is very high particularly to lime and iron rich slags.

5) Chromite Refractories

Two types of chromite refractories are distinguished:

- Chrome-magnesite refractories, which usually contain 15-35 percent Cr^2O^3 and 42-50 percent MgO. They are made in a wide range of qualities and are used for building the critical parts of high temperature furnaces. These materials can withstand corrosive slags and gases and have high refractoriness.
- Magnesite-chromite refractories, which contain at least 60 percent MgO and 8-18 percent Cr^2O^3. They are suitable for service at the highest temperatures and for contact with the most basic slags used in steel melting. Magnesite-chromite usually has a better spalling resistance than chrome-magnesite.

6) Zirconia Refractories

Zirconium dioxide (ZrO_2) is a polymorphic material. It is essential to stabilize it before application as a refractory, which is achieved by incorporating small quantities of calcium, magnesium and cerium oxide, etc. Its properties depend mainly on the degree of stabilization, quantity of stabilizer and quality of the original raw material. Zirconia refractories have a very high strength at room temperature, which is maintained up to temperatures as high as 1500^0C. They are therefore useful as high temperature construction materials in furnaces and kilns.

6) Zirconia Refractories

The thermal conductivity of zirconium dioxide is much lower than that of most other refractories and the material is therefore used as a high temperature insulating refractory. Zirconia exhibits very low thermal losses and does not react readily with liquid metals, and is particularly useful for making refractory crucibles and other vessels for metallurgical purposes. Glass furnaces use zirconia because it is not easily wetted by molten glasses and does not react easily with glass.

7) Alumina Refractories

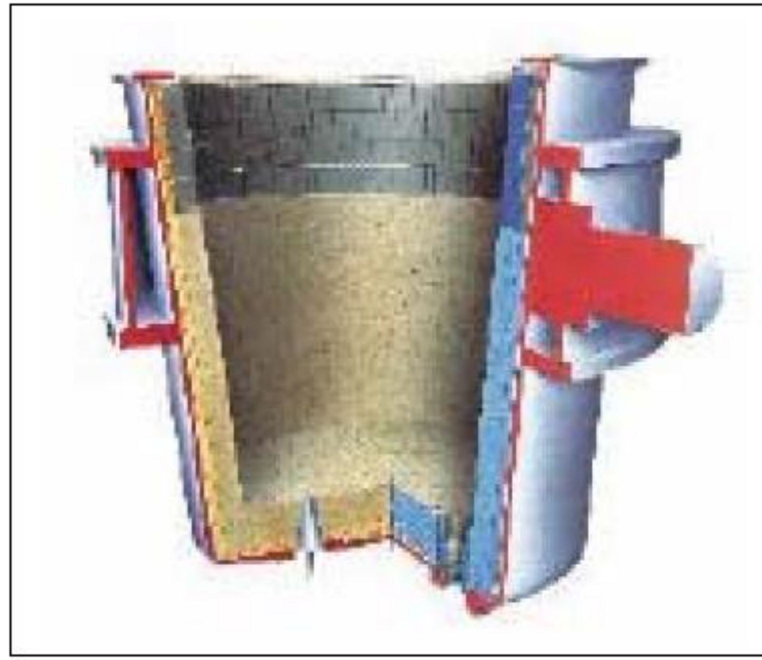
Alumina refractory materials that consist of aluminium oxide with little traces of impurities are known as pure alumina. Alumina is one of the most chemically stable oxides known. It is mechanically very strong, insoluble in water, super heated steam, and most inorganic acids and alkalies. Its properties make it suitable for the shaping of crucibles for fusing sodium carbonate, sodium hydroxide and sodium peroxide. It has a high resistance in oxidizing and reducing atmosphere. Alumina is extensively used in heat processing industries. Highly porous alumina is used for lining furnaces operating up to 1850^{o}C.

8) Monolithic Refractories

Monolithic refractories are single piece casts in the shape of equipment, such as a ladle as shown in Figure 9. They are rapidly replacing the conventional type fired refractories in many applications including industrial furnaces. The main advantages of monolithics are:

- Elimination of joints which is an inherent weakness
- Faster application method
- Special skill for installation not required
- Ease of transportation and handling
- Better scope to reduce downtime for repairs
- Considerable scope to reduce inventory and eliminate special shapes

8) Monolithic Refractories



- Heat savings
- Better spalling resistance
- Greater volume stability

Monolithics are put into place using various methods, such as ramming, casting, gunniting, spraying, and sand slinging. Ramming requires proper tools and is mostly used in cold applications where proper consolidation of the material is important. Ramming is also used for air setting and heat setting materials. Because calcium aluminate cement is the binder, it will have to be stored properly to prevent moisture absorption. Its strength starts deteriorating after 6 to 12 months.

Basic Steps in Refractory Brick Production

1. **Crushing**: Raw material in the form of big lumps are crushed to about 25 mm size.
2. **Grinding**: The crushed material are grinded in grinding machine down to 200 mesh size.
3. **Screening**: Purify the refractory raw materials and remove unwanted materials from the raw materials and this is done by
   - (a) settling
   - (b) magnetic separation
   - (C) Chemical Methods
4. **Storage**: After screening and mineral dressing, pure material is stored in storage bins with bucket elevators.
5. **Mixing**: It is done so that proper distribution of the plastic materials throughout the mass takes place. This makes moulding easier.
6. **Moulding**: Moulding may be done either manually or mechanically by the application of high pressure.

   Hand- moulding produces refractories of low density and low strength.

   Mechanical- moulding produces refractories of high density and strength.

In order to increase the density and strength of refractory by mechanical moulding, the de-airing of refractory material is essential.

De-airing is done by:

(i) Applying vacuum through vents in the moulds

(ii) by allowing air inside the void space in the refractory to go out by decreasing the rate of pressure application and release of air.

(iii) By double-pressing: the material is first pressed and allowed to crack. Then, it is pressed again so as to close the voids.

7. Drying: Removal of moisture is done under well set conditions of humidity and temperature, depending upon the type of refractories. Drying is usually carried out in tunnel dryers.

8. Firing: To stabilize and strengthen the structure of refractories, Firing is done. The bricks are , generally, fired at a temperature as high as or higher than their use temperature. It is done in tunnel Kilns or Shaft Kilns or rotary kilns.