Properties of refractory

A suitable selection of the refractory lining material for a furnace can only be made with an accurate knowledge of the chemical and physical properties of the refractories and refractory materials, and of the stresses of the materials during service. There are four types of stresses which refractories face during their period of service. These are given below:

- **Thermal :** The important properties for thermal stresses are pyrometric cone equivalent (PCE), refractoriness under load (RUL), Thermal expansion under load (creep), hot modulus of rupture, thermal expansion, reheat change (after-shrinkage and after-expansion) and thermal shock resistance.
- **Thermo-technical :** The important properties for thermo-technical stresses are thermal conductivity, specific heat, bulk density, melting point, thermal capacity and temperature conductivity.
- Mechanical ? The important properties for mechanical stresses are cold modulus of rupture and deformation modulus, crushing strength, abrasion resistance, porosity and density.
- **Chemical :** The important properties for chemical stresses are chemical composition, mineralogical composition and crystal formation, pore size distribution and types of pores, gas permeability and resistance to slag, glass melts, gases and vapours.

Some of the important physical and chemical properties are given below:

Melting point : Melting point (melting temperatures) specify the ability of materials to withstand high temperatures without chemical change and physical destruction. The melting points of major elements that constitute refractory composition in pure state vary from 1700 deg C to 3480 deg C. The melting point serves as a sufficient basis for considering the thermal stability of refractory mixtures and is an important characteristic indicating the maximum temperature of use.

Size and dimensional stability : The size and shape of the refractories is an important feature in design since it affects the stability of any structure. Dimensional accuracy and size is extremely important to enable proper fitting of the refractory shape and to minimize the thickness and joints in construction.

Porosity : Porosity is a measure of the effective open pore space in the refractory and is expressed as the average percentage of open pore space in the overall refractory volume. The mechanical strength of a refractory material is largely determined by the true porosity which is composed of closed pores and open pores, the latter being either permeable or impermeable. For higher mechanical strength, low porocity of the refractory bricks is aimed. The important properties with respect to porosity is its behaviour during chemical attack by molten metal, slag, fluxes and vapour which can penetrate and thereby contribute to degradation of the refractory structure. High porosity materials tend to be highly insulating as a result of high volume of air they trap. The content of open pores of a brick is calculated from the water absorption. By using the water air displacement method, the open pores are classified either as permeable or effective or as impermeable pores.

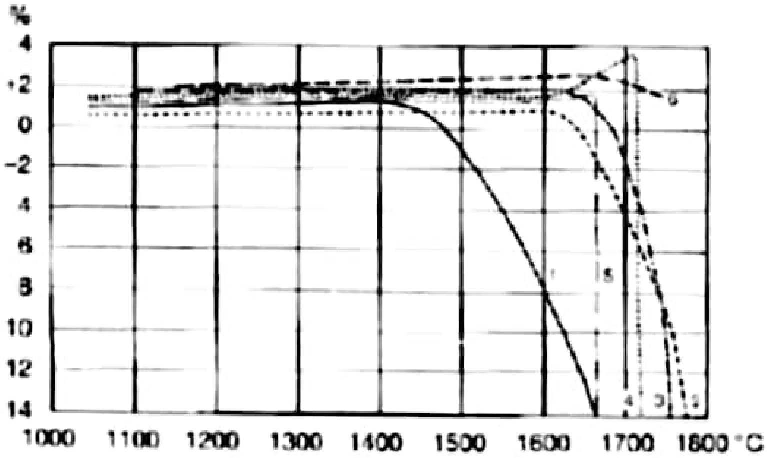
Bulk density : The bulk density (BD) is generally considered in conjunction with apparent porosity. It is a measure of the weight of a given volume including the pore space of the refractory. It is one of the important characteristic and provides a general indication of the product quality. An increase in bulk density increases the volume stability, the heat capacity, the resistance to abrasion and slag penetration. The bulk density is determined by means of a hydrostatic scale, according to the mercury displacement method or by measurement.

Cold crushing strength : It is a measure of the mechanical strength of the refractory brick. In furnaces, cold crushing strength (CCS) is of importance, because of bricks with high crushing strength is more resistant to impact from rods or during removal of slag than a brick with a low CCS. It is a useful indicator to the adequacy of firing and abrasion resistance in consonance with other properties such as bulk density and porosity.

Pyrometric cone equivalent : It is the measurement of the refractoriness. Pyrometric cone eqquivalent (PCE) is the ability to withstand exposure to elevated temperature without undergoing appreciable deformation. Refractories due to their chemical complexity melt progressively over a range of temperature. This softening behavoiour of the refractories is determined by PCE which consists of comparing ceramic specimen of known softening behaviour (seger or orton cones) with the cone of the refractory. Pyrometric cones are small triangular ceramic prisms that when set at a slight angle bend over in an arc so that the tip reaches the level of the base at a particular temperature if heated at a particular rate. The bending of the cones is caused by the formation of a viscous liquid within the the cone body, so that the cone bends as a result of viscous flow. PCE is measured by making a cone of the refractory and firing it until it bends and comparing it with standard cone. PCE is useful for the quality control purpose to detect variations in batch chemistry that changes or errors in the raw material formulation. Refractoriness points to the resistance of the refractory to the extreme conditions of heat (> 1000 deg C) and corrosion when hot and molten materials are contined while being transported and/or processed. PCE cones befroe and after firing is shown at Fig. 1

Fig 1 PCE cones before and after firing

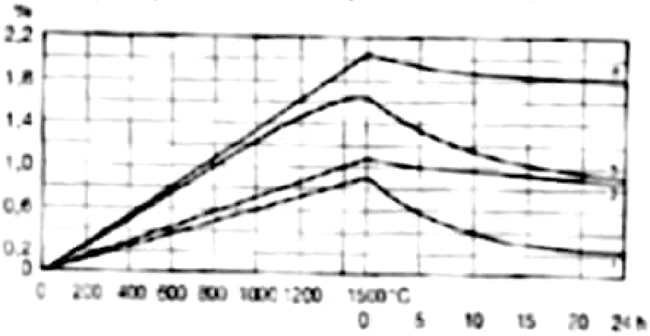
Refractoriness under load : Refractoriness under load (RUL) evaluates the softening behaviour of fired refractory bricks at rising temperature and constant load conditions. RUL gives an indication of the temperature at which the brick will collapse in service condition with similar load. However, under actual service conditions the bricks are heated only on one face and most of the load is carried by the relatively cooler rigid portion of the refractory bricks. Hence, the RUL test gives only an index of refractory quality, rather than a figure which can be used in a refractory design. Under service conditions, where the refractory used is heating from all sides such as checkers, partition walls etc. the RUL test data is quite significant. For RUL, samples in cylindrical shape of 50 mm height and 50 mm diameter are heated at a constant rate under a load of 0.2 N/Sqmm and the change in height includes the thermal expansion and also the expansion of test equipment. The test results are taken from the recording. The initial temperature is taken at 0.6 % compression while the final temperature is taken at 20 % compression or when the specimen has collapsed. RUL curves of different refractories are at Fig 2



Refractoriness under load curves of refractory bricks
1. Fireclay, 2. Sillimanite, 3. Chrome magnesia, 4. Silica (crown),
5. Silica (Coke oven), 6. Magnesia chrome

Fig 2 ? RUL curves of different refractories

Thermal expansion under load (Creep) : Thermal expansion under load (Creep) is a time dependent property which determines the deformation in a given time and at a given temperature by a refractory under stress. Refractory material must maintain dimensional stability under extreme temperatures (including repeated thermal cycling) and constant corrosion from hot liquid and gases. In the creep test, specimen of 50 mm diameter and 50 mm height with an internal bore for the measuring rod is heated at constant rate and under a given load (generally at 0.2 N/Sqmm). After the required temperature is reached, the samples is held for 10 -50 hours. The compression of the specimen, after maximum expansion has been attained, is given in relation to the test time as a measure of creep at a specified test temperature. Creep curves of refractories are at Fig 3



Creep curves of refractory bricks at 1500° C

1. **High alumina bricks with about 65 % Al2O3**
2. **High fired corundum brick with about 98 % Al2O3**
3. **High fired magnesia- chrome brick with about 10 % Cr2O3**
4. **Low iron magnesia brick with about 95 % MgO**

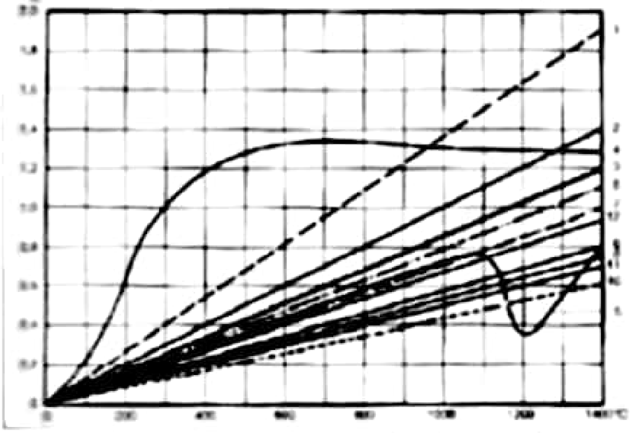
Fig 3 Creep curves of refractories

Volume stability, expansion and shrinkage at high temperature : Permanent change in the dimension of a refractory due to contraction and expansion during service can take place due to

- The changes in the allotropic forms which cause a change in specific gravity.
- A chemical reaction which produces a new material of altered specific gravity.
- The formation of a liquid phase
- Sintering reactions
- Due to fluxing by dust and slag or by the action of alkalis in case of fireclay refractories.

After heating to high temperatures and subsequent cooling, a permanent change in dimensions often occurs. This can cause either loosening of bricks during service or the destruction of brickwork due to the pressure. Permanent linear change (PLC) on heating and cooling of the refractory bricks give an indication of volume stability of the brick as well as the adequacy of the processing parameters during manufacture. It is particularly significant as a measure of conversion achieved in the manufacure of silica refractories.

Reversible thermal expansion : Refractories like any other materials expands when heated and contracts when cooled. The reversible thermal expansion is a reflection on the phase transformation that occurs during heating and cooling. The PLC and the reversible expansion are followed in the design of refractory lining for provision of expansion joints. As a rule, those with a lower thermal expansion co-efficient are less susceptible to spalling.



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.

Fig 4 Thermal expansion of different refractories

Thermal conductivity : Thermal conductivity is defined as the quantity of heat that will flow through a unit area in direction normal to the surface area in a defined time with a known temperature gradient under steady state conditions. It indicates general heat flow characteristics of the refractory and depends upon the chemical and mineralogical composition as well as the application temperature. High thermal conductivity refractories are needed for some applications such as coke ovens, regenerators etc. On the other hand refractories with lower thermal conductivity are preferred in most application since they help in conserving heat energy. Porosity is an important factor in heat flow through refractories. The thermal conductivity of a refractory decreases on increasing its porosity. Although it is one of the least important properties as far as service performance is concerned, it evidently determines the thickness of the brickwork.

Thermal shock resistance : It characterizes the behaviour of refractories to sudden temperature shocks. Temperature fluctuations can reduce the strength of the brick structure to a high degree and can lead to disintegrtaion or spalling in layers There are several methods of determining the thermal shock resistance each having its own advantages and disadvantages.

Specific heat : The specific heat is a material and temperature related energy factor and is determined with the help of calorimeters. The factor indicates the amount of energy (calories) needed to raise the temperature of one gram of material by 1 deg C. Compared to water, the specific heats of refractory materials are very low. These values are less than one fourth of value of specific heat of water.

Abrasion resistance : The mechanical stress of refractory bricks is not caused by pressure alone, but also the abrasive attack of the solid raw materials as it slowly pass over the brickwork and by the impingement of the fast moving gases with fine dust particles. Therefore the cold crushing strength is not alone sufficient to characterize the wear of the refractories. There is no approved method for testing abrasion resistance but there are some methods available to give reference values such as Bohme grinding machine method and sand blast method etc.

Modulus of Rupture or Modulus of deformation : During thermal stress, generally combined with altered physical-chemical conditions because of infiltration, strain conditions occur in refractory brickwork which can lead to brick rupture or crack formation. In order to determine the magnitude of rupture stress, the resistance to deformation under bending stress (rupture strength) is measured. Determination of the modulus of deformation in the cold state is carried out, together with modulus of rupture, on a test bar resting on two bearing edges. In general, a high ductility is looked for in refractory bricks,i.e. a large deformation region without rupture, which means a high value of the ratio of modulus of rupture to modulus of deformation.

The modulus of rupture is defined as the maximum stress of a rectangular test piece of specific dimensions which can withstand maximum load until it breaks, expressed in N/Sqmm. For hot modulus of rupture (HMOR) load is applied at a high temperature. The international standard test method is described in ISO 5013 with test piece dimensions of 150 mm x 25 mm x 25 mm.

Mineralogical composition and crystal formation : The behaviour of refractories of identical composition also depends on the type of raw materials used and on the reactions achieved during firing of the bricks. A glassy phase is more susceptible to attack by slag than a tightly interlocked crystal lattice structure. Two methods are used to identify mineralization composition. In the first method polarizing microscope or scanning electron microscope (SEM) is used. In the second method X-ray diffraction analysis is done.

Classification of refractory

Alumina bricks (or) Fire clay bricks (Acidic refractories)

Alumina bricks contain 50% or more of Al2O3. They are generally manufactured by mixing calcined bauxite (Al2O3) with clay binder.

Manufacture

1. Grinding and mixing

The raw materials (calcined bauxite & SiO2) and grog (calcined fire clay) are ground to fine poeder and mixed and mixed with required amount of water to convert it into pasty material.

2. Moulding

The pasty material is converted into bricks by the general moulding technique like machine pressing or slip casting.

3.Drying and Firing

The bricks after moulding is dried slowly to remove the moisture and then fired in continuous kiln or tunnel kiln to about 1200-1400 for 6-8 days.

Properties

(i) Alumina bricks are acidic refractories.
(ii) They posses very low coefficient of expansion.
(iii) They also posses high porosity, and high temperature load-bearing capacity.
(iv) They are also very stable to both in oxidizing and reducing conditions.
(v) Then posses better resistance to thermal to thermal spalling than silica bricks.

Uses

1. Medium-duty bricks (containing 50 to 60% Al_2O_3)

It is used in lining of cement rotary kilns soaking pita, reheating furnaces, hearts and walls, etc., which are subjected to high abrasion.

2. High-dury bricts (containing 75% Al_2O_3)

It is used in hottest zone of cement rotary kilns, lower parts of soaking pits, brass melting reverberatories, aluminium melting furnaces, etc.,

3. Fire clay refractories are larely using in steel industries

Magnesite bricks (Basic refractories)

Mangesite bricks contain mainly MgO. They are generally manufactured by mixing calcined magnesite with caustic magnesia or iron oxide as binding material.

Manufacture

1. Grinding and mixing

The raw materials (calcined magnesite) and binding materials (caustic magnesia) are ground to fine powder and mixed with water to a pasty material.

2. Moulding

Moulding is usually done by machine pressing to a required shape.

3. Drying and firing

Drying is carried out at ordinary temperature to remove the moisture. Firing is done in a kiln at 1500oC for 8 hours and then cooled slowly.

Properties

1. Magnesite bricks are basic refractories.
2. They can be used upto 2000oC without load and upto 1500oC Under a load of 3.5 kg/cm2.
3. They have good resistance to basic slags, but combine with H_2O and CO_2
4 . They possess good strength, little shrinkage and have lot of spalling.
5. They have poor resistance to abrasions.

Uses

1. They are used where high temperature is required to be maintained, together with great resistance to basic materials.
2. They are used in steel industry for the lining of basic converters and and open ?hearth furnaces.
3. They are also used in hot mixer linings, copper converters and reverberatory furnaces.

Zirconia bricks (Neutral refractories)

Manufacture

They are prepared by mixing zirconite mineral (ZrO_2) with colloidal zirconia or alumina as binder and finally heated to 1700oC. Small amount of MgO or Cao is added as stabilizer because mineral zirconite undergoes volume changes on hearting and cooling.

Properties

1. Zirconia bricks are neutral refractories.
2. Though zirconia bricks are neutral, they are affected by acidic slags.
3. They can be used upto 2000oC and upto 1500oC under a load of 3.5 kg/cm2 .
4. They are also quie resistant to thermal shocks.
5. Their thermal expansion is low.

Uses

They are used only where very high temperature is maintained, e.g., high ? frequency electric furnaces.