CERAMIC INDUSTRIES

INTRODUCTION

Ceramic is an inorganic, nonmetallic solid prepared by the action of heat and subsequent cooling. Ceramic materials may have a crystalline or partly crystalline structure, or may be amorphous (e.g. glass). Because most common ceramics are crystalline, the definition of ceramic is often restricted to inorganic crystalline materials, as opposed to the non-crystalline glasses.

The earliest ceramics were pottery objects made from clay, either by itself or mixed with other materials, hardened in fire. Later ceramics were glazed and fired to create a coloured, smooth surface. Ceramics now include domestic, industrial and building products and art objects. In the 20^{th} century, new ceramic materials were developed for use in advanced ceramic engineering; e.g., in semiconductors.

The word "ceramic" comes from the Greek word Keramos means burnt stuff. Earlier the term ceramic was applied to products made from natural earth material that was not exposed to heat. But nowadays the silicate mainly used in the construction industries and prepared by burning the clay products are called as ceramics.

CLASSIFICATION

A broad sense classification divides the ceramic products in to two classes

1. Heavy clay products e.g. bricks, roofing tiles, drain tiles, hollow tiles, stoneware and refractories
2. Pottery products e.g. chinaware, wall tiles, electric insulation

Ceramic may also be classified as porous and non-porous. The porosity is depends on particle size, moulding pressure and temperature of vitrification.

Further, ceramic may be classified based on the method of production and its uses into following classes.

1. Whiteware
2. Structural clay products
3. Refractory material

4. Special ceramic products
5. Vitreous enamel

RAW MATERIAL

The raw materials for ceramics are divided into following groups.

a) Plastics material such as clay
b) Fluxes such as feldspar
c) Non-plastics materials such as silica

a) Clay

Clay gives the main body to the ceramics. The advantage of using clay are it is plastic when mixed with water becomes hard after drying and finally it becomes irreversibly solid after firing. Clay is chosen according to the requirements of particular products and is often blended.

Impurities in common clay incorporate specific qualities as follows.

- Iron oxide in common clay gives red colour to the burnt material
- Lime, magnesia, iron oxide and alkali oxides act as flux which lowers the fusion point of clay
- Silica increases its porosity and refractory nature, while decreases shrinkage
- Clay containing very little and good deals of silica known as fire clays

b) Feldspar

Feldspar is general name given to the group of minerals. Flux materials like feldspar ($Na_2OAl_2O_3.6SiO_2$) which is easily melting material decreases the melting point of sand or quartz present in the ceramic body. So, that after firing glass like material is obtained called as vitrified material, which is highly impervious and stable to the environment. Fluxes are used for adding vitrifications, reducing porosity, to increase the strength of cold articles and for bonding. Feldspar is used as fluxing constituent in ceramic formulations along with clay. The common fluxing agents which lower the temperature are borax, boric acid, soda ash, sodium nitrate, potassium carbonate, calcined bones, lead oxides, lithium & barium minerals.

Type of feldspar

- Potash feldspar $K_2O.Al_2O_3.6SiO_2$
- Soda feldspar $Na_2O.Al_2O_3.6SiO_2$
- Lime feldspar $CaO.Al_2O_3.6SiO_2$

The physical and chemical properties of ceramic depend upon component present in it.

- The strength is mainly controlled by the factors like temperature, size and shape, composition, surface condition and microstructure
- Mechanically they are brittle and highly resistant to compression
- Oxides and carbides which give high chemical and physical stability
- Electrical and magnetic properties are due to composition itself. E.g. oxides are generally bad conductors where the non-oxides are semiconductors and ceramics with transition metal ions shows the magnetic properties.
- Transparency depends upon the crystal lattice of ceramic which in turn is dependent of composition, crystal structure, extent of polarization etc.

USES

Ceramic is one of the oldest materials used in construction with the time quality and decoration has been added to its property and therefore they are at present used in following

- Construction and decoration as bricks and tiles
- Metallurgy as construction material of furnace
- Chemical products as stoneware and porcelain
- In drainage of water
- In sanitation

The small uses includes pottery work, specialty ceramic like peuzo electric and insulation material in electrical connections

Therefore, we conclude that ceramics deals with manufacture and technical characteristics and raw material for article building.

GLASS INDUSTRIES

INTRODUCTION

When silica or quartz is heated up to 1650^{0}C it melts to a colourless liquid which on cooling gives glass. This fused mass is highly sensitive to temperature change therefore it requires special heat treatment so that ordinary glass can be manufacture which is much stable to temperature change. The glass of various commercial qualities is prepared by heating sand or quartz along with metal oxide or carbonates.

TYPES OF GLASSES

1. **Soda-lime or soft glasses**

The raw materials are silica (sand), calcium carbonate and soda ash. Their approximate composition is $Na_2O.CaO.6SiO_2$. About 90% of all glasses produced belong to soda lime glass. The low cost, low melting point soda-lime glass has resistant to de-vitrification and to water. However, they have poor resistance to common reagents like acids.

Uses: They are used as window glass, electric bulbs, plate glass, bottles, jars, building blocks and cheaper tablewares, where high temperature resistance and chemical stability are required.

2. **Potash-lime or hard glasses**

Silica (sand), calcium carbonate and potassium carbonate are the basic raw material for potash lime glass. Their approximate composition is $K_2O.CaO.6SiO_2$. They possess high melting point, fuse with difficulty and have good resistance to acids, alkalis and other solvents compare to ordinary glasses.

Uses: These glasses are costlier than soda-lime glasses and are used for chemical apparatus, combustion tubes, etc., which are to be used for heating operations.

3. **Lead glass or Flint glass**

Instead of calcium oxide, lead oxide is fused with silica. As much as 80% of lead oxide is incorporated for dense optical glasses. In addition, K_2O is used instead of sodium oxide. So, its approximate composition is $K_2O.PbO.6SiO_2$. Lead glass is more expensive than ordinary lime-soda glass, but it is much easier to shape and to work with. Lead glass has a lower softening temperature and higher refractive index than soda glass. It has excellent electrical properties. It is bright, lustrous and possesses high specific gravity (3 to 3.3).

Uses: Lead glasses are used for high quantity table wares, optical lenses, neon sign tubing, cathode ray tubes, electrical insulators and in the art objects because of their high luster. High lead content glasses are used for extra dense optical glasses, for windows and shields to protect personnel from X-rays and gamma rays in medical and atomic energy fields respectively.

4. **Borosilicate glass or Pyrex glass or Jena glass**

It is the most common of the hard glasses of commerce which contain virtually only silica and borax with a small amount of alumina and still less alkaline oxides. Borosilicate glass has the following composition.

Component	SiO_2	B_2O_3	Al_2O_3	K_2O	Na_2O
Percentage	80.5	13	3	3	0.5

Boron and aluminium oxides substitutes Na_2O and CaO used the lime-soda glasses which results in a glass of low thermal coefficient of expansion, and high chemical resistance. Borosilicate glasses have a very much higher softening point and excellent resistivity to shock.

Uses: They are used in pipelines for corrosive liquids, gauge glasses, superior laboratory apparatus, kitchenwares, chemical plants, television tubes, electrical insulators etc.

5. **96% Silica glass**

It is produced and shaped as typical borosilicate glass, having dimensions bigger than desired. The heat treatment to the article, separate the glass into two layers, one consisting mainly of silica and the other of the alkali oxides and borates. Then article is dipped in hot acid which dissolves away the alkali oxides and boron oxide layer, leaving behind a fine porous structure consisting of about 96% silica, 3% B_2O_3 and traces of other materials. This glass is then washed carefully and annealed to 1200^{0}C. The shrinkage of about 14% takes place and hard firm shape is produced which is almost gaslight. The translucent 96% glass, if it is so desired heated to a higher temperature and made almost transparent or clear.

It is expensive than other types of glasses. The expansion coefficient is very low which accounts for its high resistance to thermal shot. The softening temperature is about 1500^{0}C. They possess high chemical resistance to most corrosive agents. They are corroded by only HF, hot H_3PO_4 and concentrated alkaline solutions.

Uses: They are used where high temperature resistance is required and articles can be safely used at temperature up to 800°C. They are used for the constructed chemical plants, laboratory crucibles, induction furnace linings, electrical insulators.

6. **99.5% silica glass or Vitreosil**

It is produced by heating SiO_2 to its melting point (1,750°C). Because of absence of fluxing agents, it is extremely difficult to get rid of the bubbles. Shaping of the glass is difficult due to high viscosity at its working temperature. The final product is translucent. It has high softening temperature about 1650°C, compare to 96% silica glass. Its thermal expansion is very low. Due to their opaque nature, they tend to be mistaken for pipe when dirty and are, therefore, often broken accidentally.

If vitreosil glass is heated for long periods above its melting point, it finally becomes transparent and is then known as "clear silica glass". It has considerable transmission properties e.g. 1mm of this material allows no less than 93% of light to pass corresponding figure for good optical glass is only 6%.

Uses: uses are similar to 96% silica glass. It is exposed for the construction of pipelines for hot concentrated acid. Clear silica glass is used mainly for plant ware, chemical laboratory wares, electrical insulating materials, and in electrical heat furnaces.

7. **Alumino-silicate glass**

They possess exceptionally high softening temperature and having the typical constituent as follow

Component	SiO_2	Al_2O_3	B_2O_3	MgO	CaO	Na_2O & K_2O
Percentage	55	23	7	9	5	1

Uses: it is used for high pressure mercury discharge tubes chemical combustion tube, certain domestic equipment etc.

8. **Safety glass**

Thin layer of vinyl plastic is introduced between two or three flat sheets of glass and the whole is subjected to slight pressure. It is then heated till the glass layers and plastic layers merge into one another to give a sandwich. On cooling the glass becomes quite tough. When such a glass breaks it does not fly into pieces as the inner plastic layer tends to hold back the broken pieces of the glass.

Uses: It is mostly used in automobile and aero plane industries as wind shield.

9. **Optical or Crookes glasses**

They contain phosphorus and lead silicate, together with a little cerium oxide, is capable of absorbing harmful UV light. Very careful manufacturing process of heating the molten mass for prolonged time secured the homogeneity of the glass. In general optical glasses have low melting points and are relatively soft. Their chemical resistant and durability are appreciably lower than those of ordinary glasses.

Uses: Used for manufacture of lenses.

10. Polycrystalline glass or Pyroceram

It is the most recent development of producing glass by adding one or more nucleating agents to a special or convectional glass batch. Then it is shaped into desired form and subjected to controlled heat treatment.

The nucleating agents induced the formation of a large number of sub-microscopic crystalline which act as centers for further crystal growth. Crystalline glass is not ductile, but it has much greater impact strength than ordinary glass. It exhibits high strength and considerable hardness and can be formed and shaped into articles by any methods of manufacturing.

11. Toughened glass

It is made by dipping articles still hot in an oil bath, so that certain chilling takes place. There so, outer layers of the articles shrink and acquire a state of compression; while the inner layers are in a state of tension. Such a glass is more elastic and capable of withstanding mechanical and thermal shocks. When such a glass breaks, it does not fly but is reduced to fine powder.

Uses: It is used for window shields of fast moving vehicles like cars, trucks, aeroplane; window shields of furnaces, automatic opening doors and large show cases.

12. Insulating glass

It is a transparent unit prepared by using two or more plates of glass separated by 6-13 mm thick gap, field up with dehydrated air and then thematically sealing around the edges. This provides a high insulation against heat. Thus, if such a glass is used for separating apartments, it does not transmit heat and consequently the apartments will remain cool during summer and warm during winter.

Uses: It is used as thermal insulating materials

13. Wired glass

It is formed by embedding a wire mesh at the center of the glass sheet during casting due to this when glass breaks it do not fall into splinters. Additionally, it is more fire resistant than ordinary glass.

Uses: It is used mainly for making fire-resisting doors, windows, skylights, roofs

14. Laminated glass

It is made by pressing or bonding together two or more sheets /plates of glass with one or more alternating layer of bonding material like plastic resin, asphalt or synthetic rubber.

The essential qualities of the laminated glass are

- It is shatter-proof, i.e. its pieces do not fly off when suddenly broken.
- It is shock-proof, i.e. it can with stand sudden changes of temperature and pressure without breaking.

A bullet-resistant laminated glass is manufactured by pressing together several layers of glass with vinyl resins in alternate layers. Ordinary, thickness of such glass varies from 12.7 mm - 76.5 mm. Even thicker types are made for specific uses.

Uses: As safety glass in aircrafts, automobiles, helicopters, submarines. Bullet resistant lamination glass finds application in making automobile wind screens, looking windows etc.

15. Glass wool

It is a fibrous wool-like material composed of intermingled fine threads or filaments of glass which is completely free from alkali. Glass filaments are obtained by forcing molten mass of glass through small orifice of average diameter of 0.005 - 0.007mm continuously which is sent to rapidly revolving drum resulting in wool like form. It has low electrical conductivity and eight times higher tensile strength than steel. It does not absorb moisture and it is completely heat proof.

Uses: It is employed for heat insulation purpose, e.g., insulation of metal pipe lines, motors, vacuum cleaners, walls and roofs of houses. Being resistant to chemicals, glass wool is used for filtration of corrosive liquids like acids and acidic solution. It is used for electrical and sound insulation. It is also employed in air filter as dust filtering material. It is also used for manufacturing fiber-glass, by blending with plastic resins.

16. Photosensitive Glass

It is UV sensitive high alumina soda lime glass. The positive in UV region on glass is developed by thermal treatment only at 540-550°C. The desired photo activity in UV region can be obtained by admixture of high alumina soda lime glass with small amounts of Cu_2O $NaCN.SnO_2$ and abeitic acid in appropriate amounts. A blue colour is promoted by NaCN absence of tin oxide. In presence of tin oxide an impression in red is observed. By manipulation the ingredients in glass, brown and yellow images can also be possible. A potash alumina glass mixed with $LiSiO_3$, cerium and silver, salts in appropriate proportions have also been used as photosensitive glass.

17. Photochromic glass

Large number of microscopic particles of silver halides trapped in the three dimensional silicate networks in fixed concentration. On exposure light, temporary colour centers consisting of silver particles only are produced and these add quickly producing total darkness. The intensity of darkness depends upon the concentration of silver. Because reversible darkening is controlled by the radiations in the UV region quite abundant in day light, the photo blackening does not occurs markedly in the lamp light night.

18. Fiber glass

Fiber glass is nothing but molten glass process mechanically to a flexible thread of filament. A hot platinum nozzle filled with molten glass forces out the fluid in the form of a thin continuous thread which when caught by a rapidly moving disc gets converted into fiber through elongation and twist given by the disc fabrics made of glass are bad conductors of heat and electricity and are noninflammable. Hence articles made of fiber glass are fire proof.

Uses: Such type of glass is used in textiles and reinforcing and can be spun into yarn, gathered into a mat, and made into insulation and a great variety of other products may be with it.

MANUFACTURE OF GLASS

RAW MATERIAL

The raw material in manufacture of glass may be selected from the following.

Sand, soda ash, calcium oxide, fled spar, borax, magnesia, zinc, alumina, lead oxide, manganese oxide, selenium metal, broken glass, fluxes, colouring agent, reducing agent, oxidizing agent etc.

Oxide should satisfy following conditions

- Every oxygen atom must be attached with 2-4 cations e.g. SiO_2, B_2O_3, GeO_2, P_2O_5 and As_2O_5
- The oxygen polyhedral must share the corner position and not the edge.
- At least three corners of each tetrahedron must be share.

The oxides used for glass manufacture are classified into following groups

a) Network former
b) Network modifier
c) Intermediate glass formers
d) Oxidizing agent
e) Refining agent
f) Cullet
g) Colouring agent

a) Network former

These are oxides of elements which are surrounded by four oxygen atoms in the tetrahedral chain forming glass.

b) Network modifier

These are large diameter elements having higher co-ordination number. On simple melting they do not give glass but in presence of other network forming oxides they can give glassy products easily. The important network modifiers are oxides of alkali metal, alkaline earth metals, lead, zinc etc.

c) Intermediate glass formers

They do not give glass on melting but in presence of some network formers using their co-ordination number they start giving glass. E.g., Oxides of aluminum, silica

d) Oxidizing agent

Material like sodium nitrate or certain peroxides are used to reduce the colour of impurities like iron oxides and manganese oxide

e) Refining agent

To reduce or to eliminate quantity of air bubbles from molten glass refining agents like arsenic oxide or small amount of feldspar is added to glass.

f) Cullet

Waste or broken glass species are called cullet. In normal glass production 33% of charge is broken glasses. Recycling of cullet increases the rate of production.

g) Colouring agent

Metal oxide is added as colourant during manufacture of colour glasses e. g. oxides of chromium and iron give green glass while copper and cobalt give blue glass.

MANUFACTURE

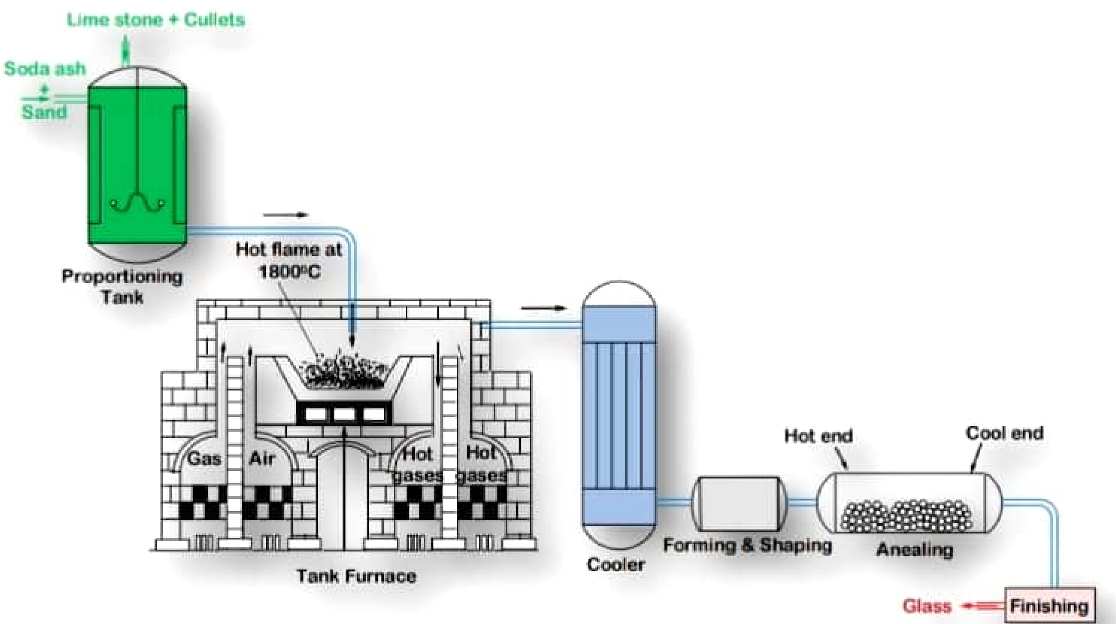

Figure : Manufacture of Glass

Block diagram of manufacturing process

Diagram with process equipment

Animation

The manufacturing process of glass consisting of the following four steps

1. Melting the charge
2. Fabrication of the article
3. Annealing the article formed
4. Finishing treatments

1. Melting of the charge

Amount of raw materials for the batch are calculated from the chemical composition of individual components. Minor ingredients are weighed accurately and given a preliminary mixing with one of the dry batch ingredients before adding to the main charge then to the batch mixer which is a revolving drum provided with blades to lift and spread the material uniformly. After proper mixing of ingredient it is charged into the furnace.

Two types furnaces are used for glass melting

a) Pot furnace
b) Tank furnace

a) Pot furnace

In pot furnace, glass is melted in open or covered pots (closed pots) of fire clay placed inside the combustion chambers of the furnace fired directly with coal (used in bangle industry) or producer gas (used tableware manufacture). Pot furnaces are generally used for small scale melting and fabrication by hand, for the production of glass bangles, table wares, lamp wares, thermos-flask etc.

b) Tank furnace

In this process, cross flame regenerative type of gas or oil used. The port is arranged along the side of the tank above the glass level those on any one side is alternatively incoming and outgoing ports.

Manufacturing large quantities of a particular type of glass tank furnace is used. E.g. manufacture of sheet glass container ware, lamp shells and resistance glasses, continuous tank furnaces are generally used.

The regeneration system consists of chambers filled with open brickwork situated on either side of the furnace, through which hot waste gases and air required for combustion pass alternatively at regular intervals of about 30 minutes. The flame acts directly upon the raw batch and molten glass. The temperature inside the furnace is generally kept at 870-985^{0}C. The molten glass kept at a constant level by continuous charging rate which is equal to the rate of withdrawal from the furnace. After withdrawal from the furnace, slow cooling of molten glass is carried to minimize permanent strain. The higher the temperature used for reheating, lesser will be time to remove the strain.

Introduction to Refractories

Refractories are material having high melting points, with properties that make them suitable to act as heat-resisting barriers between high and low temperature zones.

ASTM C71 defines refractories as "non-metallic materials having those chemical and physical properties that make them applicable for structures or as components of systems that are exposed to environments above 1000 °F (538 °C)".

Refractories are inorganic nonmetallic material which can withstand high temperature without undergoing physical or chemical changes while remaining in contact with molten slag, metal and gases. It is necessary to produce range of refractory materials with different properties to meet range of processing conditions.

Refractories are useful in constructing application-specific high temperature areas/surfaces, particularly in furnaces or boilers, as they minimize heat losses through structure.

Depending on the operating environment, they need to be resistant to thermal shock, be chemically inert, and/or have specific ranges of thermal conductivity and of the coefficient of thermal expansion.

Alumina, silica and magnesia are the most important materials used in the manufacturing of refractories. Another oxide usually found in refractories is the oxide of calcium (lime). Fire clays are also widely used in the manufacture of refractories.

Refractories must be chosen according to the conditions they will face. Some applications require special refractory materials. Zirconia is used when the material must withstand extremely high temperatures. Silicon carbide and carbon (graphite) are two other refractory materials used in some very severe temperature conditions, but they cannot be used in contact with oxygen, as they will oxidize and burn.

Refractories perform four basic functions:

1. They act as a thermal barrier between a hot medium (e.g., flue gases, liquid metal, molten slags, and molten salts) and the wall of the containing vessel.
2. They insure a strong physical protection, preventing the erosion of walls by the circulating hot medium.
3. They represent a chemical protective barrier against corrosion.
4. They act as thermal insulation, insuring heat retention.
5. The principal raw materials used in the production of refractories are: the oxides of silicon, aluminum, magnesium, calcium and zirconium and some non-oxide refractories like carbides, nitrides, borides, silicates and graphite.

What are refractories used for?

1. Refractories are used by the metallurgy industry in the internal linings of furnaces, kilns, reactors and other vessels for holding and transporting metal and slag.
2. In non-metallurgical industries, the refractories are mostly installed on fired heaters, hydrogen reformers, ammonia primary and secondary reformers, cracking furnaces, utility boilers, catalytic cracking units, coke calciner, sulfur furnaces, air heaters, ducting, stacks, etc.
3. Majority of these listed equipment operate under high pressure, and operating temperature can vary from very low to very high (approximately 900°F to 2900°F).
4. The refractory materials are therefore needed to withstand temperatures over and above these temperatures.
5. Due to the extremely high melting point of common metals like iron, nickel and copper, metallurgists have to raise furnace temperatures to over 2800°F.

Requirements of right refractory

The general requirements of a refractory material can be summed up as:

1. Its ability to withstand high temperatures with sudden changes of temperature.
2. Its ability to withstand action of molten metal, hot gasses and slag erosion etc.
3. Its ability to withstand load at service conditions.
4. Its ability to resist contamination of the material with which it comes into contact.
5. Its ability to maintain sufficient dimensional stability at high temperatures and after/during repeated thermal cycling.
6. Its ability to conserve heat.

Melting point of some pure compounds used to manufacture refractory

Compounds	Melting point (℃)
MgO (pure sintered)	2800
CaO (limit)	2571
SiC pure	2248
MgO (90-95%)	2193
Cr_2O_3	2138
Al_2O_3 (pure sintered)	2050
Fireclay	1871
SiO_2	1715

Classification of Refractories

Refractories are classified into number of ways on the basis of chemical properties of their constituent substances, their refractoriness, method of manufacture and physical form.

1) Classification Based on Chemical Composition

Refractories are typically classified on the basis of their chemical behavior, i.e. their reaction to the type of slags. Accordingly the refractory materials are of three classes - Acid, Basic & Neutral.

Acid Refractories:

Acid refractories are those which are attacked by alkalis (basic slags). These are used in areas where slag and atmosphere are acidic. Examples of acid refractories are:

1) Silica (SiO_2).
2) Zirconia (ZrO_2).
3) Aluminosilicate.

Neutral Refractories:

Neutral Refractories are chemically stable to both acids and bases and are used in areas where slag and atmosphere are either acidic or basic. The common examples of these materials are:

1) Carbon graphite (most inert)
2) Chromites (Cr_2O_3)
3) Alumina

Out of these graphite is the least reactive and is extensively used in metallurgical furnaces where the process of oxidation can be controlled.

Basic Refractories:

Basic refractories are those which are attacked by acid slags but stable to alkaline slags, dusts and fumes at elevated temperatures. Since they do not react with alkaline slags, these refractories are of considerable importance for furnace linings where the environment is alkaline; for example non-ferrous metallurgical operations. The most important basic raw materials are:

1) Magnesia (MgO) - caustic, sintered and fused magnesia
2) Dolomite (CaO.MgO) - sintered and fused dolomite
3) Chromite -main part of chrome ore

Chemical characteristics of the furnace process usually determine the type of refractory required. Theoretically, acid refractories should not be used in contact with basic slags, gases and fumes whereas basic refractories can be best used in alkaline environment. Actually, for various reasons, these rules are often violated.

2) Classification Based on Method of Manufacture

The refractories can be manufactured in either of the following methods:

a) Dry Press Process.
b) Fused Cast.
c) Hand Molded.
d) Formed (Normal, Fired or chemical bonded).
e) Unformed (Monolithic – Plastics, Ramming mass, Gunning, Cast able, Spraying).

3) 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 may be 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 joint less lining and are better known as monolithic refractories. These are categorized as Plastic refractories, ramming mixes, castables, gunning mixes, fettling mixes and mortars.