UNIT 8 GLASS AND CERAMICS

Structure

8.1 INTRODUCTION

A **glass** is an amorphous and transparent solid substance which is produced on the solidification of a liquid state without crystallization. Glass is therefore, classified as a 'supper cooled liquid' that lacks three dimensional periodicity characteristic of a crystal. *Solidification* refers to the transformation of materials from the liquid to the solid state. While cooling, the disordered structure of the liquid changes to the orderly arrangement and it is known as *crystallization*. When the disordered structure of the liquid is frozen as it is, the change is said to be a *glass transition*. Thus, glass does not have a sharp melting point. When a glass is heated, it begins to soften at a temperature far below the point at which it flows like a liquid.

Glass is obtained when white sand is fused with alkaline earth metal oxides and carbonates. Thus, it is a mixture of a number of silicates. The mixture can be represented as $x\,M_2O,\ y\,M'O\ .\ 6\,SiO_2$ for ordinary glass.

where, $M \rightarrow$ Monovalent alkaline earth metals

$M' \rightarrow$ Bivalent metals

$x, y \rightarrow$ are the simple integers

For example, it can be stated as

$$Na_2O.\,CaO\,.\,6SiO_2$$

By replacing certain metals, different glasses can be obtained.

Ceramics are inorganic, non-metallic materials (e.g. chinaware, earthware, stoneware etc.) that can be made into a paste and shaped at normal temperature to prepare different articles. The shape is then fired at a high temperature to produce strength in it by sintering the crystallites together. A number of metallic oxides, carbides, silicates, and their combination are processed in the same way to obtain different ceramics. Ceramics can be grouped broadly into three types :

(i) clay products,

(ii) glasses, and

(iii) refractories.

Objectives

After studying this unit, you should be able to

- define glass,
- describe the important raw materials used for manufacture of glass and ceramics,
- explain the different manufacturing steps,
- define solidification, crystallization, glass transition and other terms used in manufacturing steps,
- discuss the general properties of glass,
- describe different types of glasses, their properties and uses,
- explain the characteristics of solidification without crystallization,
- describe fractures and their preventive method,
- describe the manufacture of whiteware,
- explain the liquid glazing of ceramics,
- describe the preparation, properties and uses of ceramics, and
- explain the chemical conversion that takes place in the manufacture of ceramic products.

8.2 MANUFACTURE OF GLASS

The important raw materials required for the manufacture of glass are :

(i) **Silica (in the form of Sand)**

It must be uniform in size. Too coarse particles prevent them to react with other substances while too fine ones make it violent. The chief impurities (organic matter, iron, alumina etc.) must be removed from the sand.

(ii) **Compounds of Alkali Metals (Na_2CO_3, Na_2SO_4, $NaNO_3$, K_2CO_3, KNO_3)**

Sodium and potassium are introduced generally in the form of above compounds to which 5% carbon is added as a reducing agent.

(iii) **Compounds of Alkaline Earth Metals ($CaCO_3$, CaO, $BaCO_3$)**

These are required when glass of high refractive index is needed. Iron and magnesium are the general impurities in the compounds. Iron is harmful, so it has to be removed but magnesium helps to control the physical properties of glass.

(iv) **Oxides of Heavy Metals (PbO, Pb_2O_4, ZnO)**

Litharge or red lead is used as source of lead. Red lead is preferable due to high oxygen content. Oxides of iron, copper, and metallic lead should be avoided. Lead is replaced by zinc oxides along with borax to prepare heat resisting glass.

(v) **Borax or Boric Acid**

Borax lowers the coefficient of expansion of the glass and increases its durability.

(vi) **Calcium Phosphate [$Ca_3(PO_4)_2$]**

This is required when it is desired to produce opalescent glass. Arsenic and antimony can also be added in such cases.

(vii) **Alumina**

It makes glass resistant to sudden changes of temperature.

(viii) **Cullets**

These are pieces of waste glass which facilitate fusion and utilization of waste. This acts as a flux.

(ix) **Colouring Materials**

Certain metallic oxides are added to fused silicates to manufacture glass of different colours such as follows :

Red glass	→	Cu_2O
Yellow	→	Ferric oxide (Fe_2O_3)
Green	→	Chromium oxide
Purple	→	Manganese oxide
Lemon yellow	→	Cadmium sulphate
Blue	→	CuO, CaO
Milky glass	→	SnO, cryolite [$Ca_3(PO_4)_2$]
Violet	→	MnO_2
Black	→	CaO, MnO, Nickel oxide
Fluorescent greenish yellow	→	uranium oxide.

8.2.1 Manufacturing Steps

The manufacturing of glass involves the following steps :

(i) Fusion of Raw Materials

The raw materials to be used depend upon the variety of glass obtained. Raw materials in proper proportions of sodium carbonate, calcium carbonate, and sand or quartz mixed with cullets are finely powdered and mixed intimately (batch) with one another for the manufacture of ordinary soda lime glass. The mixture is then introduced into the tank furnace or pot furnace for fusion purposes. The furnace is heated by producer gas and air mixture on the generative principle of heat economy which generates temperature upto 1800^oC. The furnace is shown in Figure 8.1.

Figure 8.1

The melting process involves the evolution of gases like CO_2, SO_2, O_2 etc. The temperature is further raised upto 1800^oC so the charges melt and fuse until all gas bubbles escape. The molten glass is allowed to stand for some time (800^oC) to get homogeneous mass. The chemical reactions taking place during these processes are :

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2 \uparrow$$

$$Na_2SO_4 + C \rightarrow Na_2O + CO_2 \uparrow + SO_2 \uparrow$$

$$Na_2O + SiO_2 \rightarrow Na_2O\,.\,SiO_2$$

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2 \uparrow$$

If a coloured glass is desired, the colouring materials are added at the molten stage. Commercial glass is a mixture of a number of metallic silicates *viz.* $Na_2O\,.x\,SiO_2.Na_2O.y\,SiO_2$ and $Na_2O.z\,SiO_2$, where x, y and z are integers.

(ii) Forming and Shaping

The desired articles to be made from glass are obtained by either blowing the molten glass or moulding or pressing between rollers into definite shapes. The whole process (blowing or moulding or pressing) is to be done within few seconds.

(iii) Annealing

Annealing is a process in which the newly shaped articles are cooled slowly. If the glass is allowed to be cooled rapidly, it becomes brittle and fragile and if it is cooled very slowly, it devitrifies and becomes opaque. For better quality of glass, annealing process should be in between too rapid and very slow cooling.

(iv) Finishing

The glass articles, after annealing are subjected to finishing processes like cutting, grinding, polishing, cleaning, sand blasting etc.

8.2.2 Properties of Glasses

Glass has the following characteristics :

(i) Amorphous – means shapeless, i.e. the constituents are arranged at random in the same disorderly way as in liquids.

(ii) No sharp melting point – an amorphous substance does not have a sharp melting point.

(iii) Transparent.

(iv) Less prone to chemical attacks except hydrogen fluoride

(v) It softens on heating.

(vi) It is affected by alkalis.

(vii) It is not affected by air and water.

(viii) It has high refractive index.

(ix) It is hard and brittle.

(x) It has high compressive strength.

(xi) It is highly polished and insulator of heat and electricity.

SAQ 1

(a) What is glass? What are the functions of borax and alumina used in the manufacture of glass?

(b) The main constituent of glass is :

(i) CaO

(ii) SiO_2

(iii) Al_2O_3

(iv) Boron

8.3 GLASS TRANSITION

Glass transition is a process of solidification without crystallization, i.e. the disordered structure of the liquid is frozen as it is, to a solid state. Generally, it is very difficult to prevent crystallization of liquids which have a high freezing temperature T_m, a large value of heat of fusion Δh, and a low value of the activation enthalpy for atom transfer ΔH_d.

Silicates, phosphates and borates have greater tendency to form glass because of their open structures. Open structure refers to appreciable degree of freedom for the units surrounding a central unit which is possible due to the high cation-cation repulsion. Generally, the open structures have low heat of fusion (Δh) and the viscosity is very high (10^5 poise at the equilibrium freezing temperature). Viscosity is directly related to activation enthalpy ΔH_d.

8.3.1 Glass Transition Temperature (T_g)

Some liquids can be super-cooled to a rigid non-crystalline solid in which the viscosity continuously increases with decreasing temperature and attains the high value characteristic of a crystal only at low temperature. The highest rate of change of viscosity occurs around 10^{13} poise at the temperature T_m, called the *glass transition temperature*, as shown in Figure 8.2.

Figure 8.2 : Viscosity Changes during Cooling (Soda Lime Glass)

If a liquid crystallizes, the viscosity would change abruptly at the freezing point from a low value (about 10^{12} poise) in the liquid state to a very high value (about 10^{20} poise) in the crystalline state as is shown in above figure. In glass transitions, the cooling rate around T_g is important in the control of properties. The transition temperature is lower at a slower cooling rate and the specific volume at any temperature below the transition region is also smaller. This shrinkage of volume can lead to important errors, particularly in measuring apparatus such as glass thermometers. Such shrinkage in optical glasses can lead to non-uniformity in the refractive index. To overcome this problem, the glass should be cooled as slowly as possible through the glass transition temperature. Similarly, a rapidly cooled glass can be reheated and annealed for some time at a temperature just below T_g, to avoid future shrinkage.

8.3.2 Fracture

Fracture means the facture of a material under load by breaking into pieces which can occur under all service conditions. One of the important properties of glass is that it is hard and brittle. Thus, we shall now discuss the nature of brittle fracture and then explain the methods of preventing glasses against brittle fracture.

Brittle Fracture

This refers to the fracture of glass without prior plastic deformation. The important characteristic of this fracture is that the broken pieces can be fitted together to get the original shape and dimensions of the specimen.

8.3.3 Methods of Protection against Fracture

The surface cracks are twice as effective as internal cracks because surface cracks can effectively reduce the surface energy by chemical adsorption of molecules on the surface. The most important methods used for protection against brittle fracture are :

(i) Surface treatment method, and

(ii) Compressive stress method.

(i) **Surface Treatment Method**

In this method, the cracked surface of a glass is etched with hydrofluoric acid (HF). Thus, the surface layers and the cracks in them are removed. The freshly etched surface should be protected against further mechanical abrasion and corrosion by covering it with a polymer like epoxy in fibre reinforced plastics.

(ii) **Compressive Stress Method**

This method is suitable for tempered glass. In this method, the silicate glass is heated above its softening temperature and annealed long enough to remove all the residual stresses. Then cold air is blasted directly against the glass to cool the surface layers rapidly. They contract and become rigid, hence cracks are removed. This heat treatment is known as **tempering**.

Similar procedure can be adopted to protect against the *fatigue crack propagation*. *Fatigue crack propagation* refers to the cracks propagated from the surface inwards.

SAQ 2

(a) Explain why silicates, phosphates and borates have greater tendency to form glass.

(b) What is glass transition temperature?

(c) Name the important methods to prevent brittle fracture.

8.4 VARITIES OF GLASSES

In this section, you will study about composition, properties and uses of various types of glasses.

(i) **Soda Lime or Soft Glass**

It is a mixture of raw materials like sodium and calcium silicate $Na_2O.CaO.6SiO_2$. The approximate composition is SiO_2 75%, sodium oxide 15%, calcium oxide 8% and aluminium oxide 2% (as impurity). They soften at a comparatively lower temperature and are, thus called as *soft glass* and can be hot worked easily. These glasses are resistant to devitrification and resistant to water also.

Uses

The soda lime glass is used in making cheap window panes, electric bulbs, bottles, dishes and other substances where high temperature resistance and chemical stability are not required.

(ii) **Potash Lime or Hard Glass**

It is a mixture of potassium and calcium silicates as SiO_2, (K_2CO_3 + $CaCO_3$). Their approximate composition is $K_2O.CaO.6SiO_2$. It is a hard glass as it possesses high melting point and can withstand higher temperature and is comparatively more resistant to acid, alkali and other solvents than the soft glasses.

Uses

They are used for making hard glass apparatus for laboratories, combustion tubes and other substances where comparatively high temperature resistance and chemical stability are required.

(iii) **Flint Glass (Lead Glass)**

In this glass, lead carbonate or lead oxide is used in excess to have the composition as K_2O. PbO. $6SiO_2$. The approximate composition as silica (45%), sodium oxide (4%), potassium oxide (4%), calcium oxide (3%) and lead oxide (44%). It is prepared by fuming litharge (lead oxide), potassium carbonate and silica in proper propositions.

Properties

(i) The flint glass is of higher refracting power.

(ii) It has a higher density and transparency than ordinary glasses.

(iii) It has lower softening temperature than soda glasses.

(iv) It has excellent electrical properties.

(v) It has high specific gravity.

(vi) It is bright and lustrous.

Uses

It is used for making optical instruments, ornamental purposes, high quality table wares, neon sign tubings, cathode ray tubes, electrical insulators etc. It is also used as shields to X-rays and γ-rays in medical and atomic energy fields, respectively.

(iv) **Crown Glass**

A partial replacement of silica by phosphorous penta-oxide gives crown glass.

(v) **Pyrex Glass (Borosilicate Glass)**

It is a mixture of sodium aluminium borosilicates i.e. certain amounts of boron and aluminium oxides are mixed together to produce this most common of the hard glass of commerce. These are called as *pyrex glasses*. The approximate composition is silica 80%, sodium oxide 4%, calcium oxide 0.5%, potassium oxide 0.5%, B_2O_3 12%, Al_2O_3 3%.

Properties

(i) They have a low coefficient of expansion.

(ii) They can withstand sudden alteration of temperature very well without cracking.

(iii) They contain less alkali and so are less prone to chemical attack.

(iv) Borosilicate glasses have very high softening point and excellent resistivity (shock proof).

Uses

Such glasses are widely used for laboratory equipments which are to be heated at high temperature. They can be used in kitchenwares, chemical plants, electrical insulators etc. They are also extensively used in industry for pipelines for corrosive liquids.

(vi) **Jena Glass**

It is obtained by decreasing the alkali content and increasing the alumina content in ordinary glass. It also contains barium and zinc oxides and boron trioxide in place of some silica.

Properties

(i) It is very resistant to heat, chemicals (acid and alkali) and shocks.

(ii) This glass possesses exceptionally high softening temperatures.

(iii) This glass is stronger than the ordinary glass.

Uses

It is used in chemical combustion tubes, certain domestic equipment etc.

Properties

(i) It has very high viscosity.

(ii) Its softening temperature is as high as $1650^{o}C$.

(iii) Its thermal expansion is very low.

Uses

It is mainly used in chemical plants, laboratory wares, furnaces etc.

(vii) **Alumino Silicate Glass**

If silica is partially replaced by aluminium in ordinary glass then aluminium silicate glass is obtained. The approximate composition of this glass is: SiO_2(55%), Al_2O_3 (23%), B_2O_3 (7%), MgO (9%), CaO (5%), Na_2O (0.5%) and K_2O (0.5%).

Properties

It has very high softening temperature.

Uses

It is used in domestic equipments, chemical combustion tubes, mercury discharge tubes etc.

(viii) **Crooke's Glass (Optical Glass)**

It is generally made by fusing red lead, potassium carbonate and sand. Special varieties of Crooke's glass can be made, i.e. boron trioxide in place of silica and, barium and zinc oxide in place red lead. Crooke's glass contains cerium oxide which prevents ultraviolet light harmful to eyes.

Properties

(i) They have low melting point and are relatively soft.

(ii) They have low chemical resistance.

(iii) They have low durability.

Uses

These are used as special type of glass for optical purposes (making lens).

(ix) **Bottle Glass**

It is ordinary soda lime glass having approximate composition of MgO (3.5%). Al_2O_3 Fe_2O_3 (0.5%).

Uses

It is used as cheap commercial glass.

(x) **Ground Glass**

It is prepared by grinding ordinary soda (soft) glass by emery and turpentine oil or by sand blasting.

(xi) **Safety Glass**

It is obtained by taking two or three flat glass sheets and in between them alternative thin layers of butyral plastic or vinyl acetate resin is introduced with a suitable adhesive and cementing them by heat and pressure. On cooling, the glass becomes tough.

Properties

This glass does not break easily under ordinary impact but when it breaks it does not shatter.

Uses

It is used in making automobile wind shields, aeroplane wind shields etc.

(xii) **Laminated Glass**

Fine layer laminated glass can also be obtained in the same way as above by placing a layer of resin, asphalt or synthetic rubber with a suitable adhesive between two layers of glasses. This process is repeated for several time in order to get high thick glass which will become bullet proof.

Properties

(i) It is shatter proof and shock proof.

(ii) It withstands the sudden changes of temperature and pressure without breaking.

Uses

For making bullet proof glasses, safety aircraft and automobile glasses etc.

(xiii) **Glass Wool**

It is fibrous wood-like material which is obtained by forcing molten glass through tiny holes in presence of a jet of high pressure system and then put over a rapidly revolving drum to get the materials in wool like form.

Properties

(i) It is non-combustible and fire proof.

(ii) These are stain resistant and electrically insulator.

(iii) It has high chemical resistance and it does not absorb moisture or water.

(iv) It has low thermal conductivity and low density.

(v) It has very high tensile strength.

Uses

(i) Since it is a thermal insulator, it is used as wrapper for various articles in the form of glass wool.

(ii) It is used for making fire proof clothings.

(iii) It is used in air filters as dust filtering materials.

(iv) It is used for filtration of corrosive liquids (acids etc.) as it is resistant to chemical actions.

(v) Hollow glass bricks are used in constructing walls where light would come in but cold could be kept out.

(vi) It is used for manufacturing fibre glass, electrical insulation wares, industrial appliances, domestic wares and other articles where heat resistance is required.

(xiv) **Pyroceram (Polycrystalline Glass)**

This is special type of glass which is obtained by adding certain nucleating agents to a conventional glass by subjecting it to a controlled heat treatment and then shaping into a desired form.

Properties

(i) It is hard and has greater impact strength.

(ii) It is not ductile.

Uses

It is mainly used for sub-microscopic crystallites.

(xv) **Toughened Glass**

It is obtained by dipping the hot glass articles in an oil bath so that the outer layers of the articles shrink and acquire a state of compression; while the inner layers are in state of tension. These glasses can withstand more mechanical and thermal shocks. These are also more elastic.

Uses

It is used as window shields for automobile, automatic opening doors etc.

(xvi) **Coloured Glass**

To produce glass in different colours, various mineral substances are mixed with it during the process of manufacture.

(xvii) **Wired Glass**

It is obtained by embedding a wire mesh at the center of the glass sheet during casting. It is more fire proof than ordinary glass and hence is used in making windows, skylights, roofs etc.

(xviii) **Insulating Glass**

It is prepared by fitting up the insulating materials like dehydrated air between two or more glass plates and then thermetically sealing around the edges. The gap between the glass plates depends on the purpose of use, i.e. 6 to 14 mm thickness.

Uses

Since it is a thermal insulator, it is used in walls to make the rooms cool during summer and warm during winter.

SAQ 3

Explain why Crooke's glass finds use in making spectacle glasses.

8.5 CERAMICS

Ceramics are the most important engineering materials which can be used at high temperatures. Based on properties like plasticity, heat resistance, fracture, and abrasive and corrosive resistance, ceramics can be grouped broadly into three types :

(i) clay product,

(ii) glasses, and

(iii) refractories.

We have already discussed glasses, thus in this section we will discuss **clay products** and **refractories**.

8.5.1 Clay Products

Clay products can be subdivided into three main types :

(i) The *structural clay products* having main composition of iron oxides. They are used for bricks, tiles, and similar products.

(ii) The *whiteware* which is best known an chinaware.

(iii) *Chemical stonewares* which are very hard, resilient and non-porous. Generally, these are used for sanitary fixtures like sinks, bath-tubs, piping vessels, drainage pipes etc.

8.5.2 Clay

The clay is composed essentially of hydrated aluminium silicates together with other substances such as mica, quartz, cherts and flints. Some common clays are :

(i) Kaolin $\rightarrow$ $Al_2O_3.2SiO_2.2H_2O$

(ii) Beidellite $\rightarrow$ $Al_2O_3.2SiO_2.H_2O$

(iii) Halloysite $\rightarrow$ $Al_2O_3.SiO_2.3H_2O$

Clay is used for manufacture of whiteware due to its following properties :

(i) It is plastic and can be moulded when it is wet.

(ii) It retains its shape when dried.

(iii) When moulded mass is heated to a high temperature, it sinters together forming a hard coherent mass without losing its original colour.

Plasticity

The plasticity of clay refers to its ability to form a plastic mass with water, so that it can be moulded easily to any desired shape, but retains sufficient rigidity to prevent deformation on standing. Every clay has certain water retention capacity below which it does not behave as plastic and becomes crumbly. This is called the **plastic limit** of a clay. The maximum point of water retention capacity of clay is known as **liquid limit**. The **plasticity index** is the difference between liquid limit and the plastic limit.

$$\text{Plasticity index} = \text{Liquid limit} - \text{Plastic limit}$$

Different moulding methods employed to get different degree of plasticity are :

(i) **Hand-moulding and Machine Extrusion :** In this method stiff mud is obtained which is characterized by plastic consistency.

(ii) **Machine Pressing :** In this method, stiff plastic and semi dry mixed is obtained.

(iii) **Stip Casting :** Mix of semi liquid consistency is required.

The required plasticity can be obtained by :

(a) **Weathering and Grinding :** This method is employed to improve the plasticity and homogeneity of the mass.

(b) **Blending :** Blending is a process in which some agents or ingredients are added in a certain proportions to get desirable plasticity of the clay. For example :

(i) Fluxes, the easily fusible materials like borax, boric acid, soda ash, Pearl ash (K_2CO_3), Fluorspar (CaF_2), Cryolite ($Na_2\ AlF_6$), iron oxide etc. are added to a mix to lower its fusion point to get complete vitrification.

(ii) Sand (SiO_2) or flint is used as an opener for reducing the shrinkage of the clay.

(iii) Felspar or spar serves as a flux as well as a binder for the clay particles. It is a double silicate of K or Ca with Al. Some common felspar are (a) Potash Felspar ($K_2O.Al_2O_3.6SiO_2$). (b) Soda Felspar ($Na_2O.Al_2O_3.6SiO_2$), (c) Lime Felspar ($CaO.Al_2O_3.6SiO_3$).

8.5.3 Whitewares

The clay materials which produce the white or pale cream coloured products after firing are called as *whitewares*. China clay, felspar and flint are the important raw materials required for the manufacture of white wares. The raw materials contain little or no compounds of iron. These raw materials are mixed in a certain proportion to obtain the desired finished article.

Manufacture of Whitewares

The following steps are followed for the manufacture of whitewares :

Preparation of Slip

Slip is a paste like substance which is obtained by mixing and continuous stirring the raw materials in a suitable proportion with water. Then, it is filtered to remove the coarse particles, if any.

Filtering and Aging

To remove the water particles, the filtered slip is passed through the filter paper. This moist cake (10 to 30% water) is stored for few weeks to remove all the moisture. This process is known as *aging*. This process increases the plasticity of the clay.

Shaping of the Articles

Hand-moulding or machine pressing methods are used for shaping of the articles. Na_2CO_3 or K_2CO_3 or water glass is added to the clay to get the cast. Then the article so produced is dried slowly and fired to the desired density in a biscuit over to get porous were called **bisque**.

With these three steps, we can get the body of ware. Then the following steps are carried out obtain the finished products.

(a) **Firing**

The dried articles are placed into hovel oven in saggers of firing to avoid direct contact with flame. During the process of firing, the following chemical changes occur at different temperatures.

Sl. No.	Temperature	Chemical Changes Occurred
1	At $150^o – 600^oC$	Water is completely removed.
2	At $800^o – 900^oC$	Lime stone gets decomposed ($CaCO_3 \rightarrow CaO + CO_2 \uparrow$)
3	At $350^o – 900^oC$	Oxidation of ferrous salt and organic matter occurs.
4	At $1200^o – 1300^oC$	Combination of metallic oxides with silica (SiO_2). Thus, silicates of different metals may be formed.

The products obtained by this method are porous like a biscuit and hence is called **biscuit**.

(b) **Glazing of the Biscuit**

In order to get impervious articles to liquid, a glaze may be employed by melting it over the surface or body. *Glaze* is a mixture of glass forming materials *viz*. SiO_2, Al_2O_3, lead oxide, ceric oxide, borosilicates etc. and atleast one alkaline metal. This mixture should be free from iron and other colouring pigments. For colour glazing, coloured metal oxides may be mixed in proper proportions.

- **Purpose of Glazing**

  Glazing is mainly applied on the earthware to fulfill the following requirements.

  (i) To make the earthware surface impervious to liquids.

  (ii) To increase the durability of ceramic materials.

  (iii) To produce coloured and decorative effects.

  (iv) To provide smooth and shining surface to treated materials.

  (v) To protect the surface from corrosive action by the environment.

- **Methods of Glazing**

  Dipping, pouring, spraying, dusting, volatilisation, immersion etc. are the various methods of applying the glazes on the articles. All these methods can be broadly categorized into two types (i) salt glazing (solid form), and (ii) liquid glazing (liquid form).

  (i) **Salt Glazing**

  In this process, common salt like NaCl or KCl is poured into the furnace where due to intensive heat (700^o to 900^oC) these salts volatize and react with silica of the article to form glossy or shinning and impervious film of sodium potassium silicate.

  (ii) **Liquid Glazing**

  In this method, glaze slip is prepared by mixing the fine powder of glaze mixture, suitable proportion of colouring pigments, and desired quantity of water with continuous stirring. The articles to be glazed are heated in hovel oven at 350^o to 500^oC temperature. Then these hot articles are dipped into the glaze slip. Again these articles are fired in the oven at 700^o to 900^oC to obtain smooth, shining and impervious film to liquid products.

(c) **Colouring of the Article**

At the preparation of glaze step, the desired colour pigments may be added. The materials used as colouring agents are :

(i) Cobalt oxide $\rightarrow$ Blue

(ii) Chromium $\rightarrow$ Green or red.

(iii) Copper oxide $\rightarrow$ Green or red

(iv) Iron oxide $\rightarrow$ Yellow, orange or red.

(v) Gold chloride $\rightarrow$ Pink

(vi) $TiO_2 \rightarrow$ Faint yellow.

(vii) $MnO_2 \rightarrow$ Violet.

Properties of Whitewares

(i) They have very low porosity and good transparency, and

(ii) They possess good strength.

Uses

Used as insulators, laboratory equipments, crucibles, dishes, high class potteries and domestic utensils etc.

8.5.4 Earthenware and Stoneware

The earthenware and stoneware are basically clay products and the manufacturing process for both the wares are almost same as the manufacturing process of whitewares. The earthenware are comparatively softer whereas the stoneware are very strong and hard like stone. Glazes are also required to obtain smooth and shinning products. The approximate composition of stoneware is clay 50%, kaolin 5%, felspar 20%, flints 15%, scrap stoneware 10%.

Properties

(i) Stoneware have low absorption power.

(ii) They have high density and are semi vitrified.

(iii) They are comparatively more chemical resistance and having more physical or impact strength.

(iv) They are resistant to acids and alkalis.

Uses

These are mainly used for sanitary fixtures like sinks, bath-tubs, drainage pipes, piping vessels etc.

SAQ 4

(a) Explain the liquid glazing of ceramics.

(b) What are ceramics and how are they classified?

(c) What is the plasticity of clay?

8.6 REFRACTORIES

The refractory materials are those which can withstand high temperature at least $600^{o}C$ in the furnace without melting, softening or suffering a deformation in shape. Some important refractories are Al_2O_3, FeO, Cr_2O_3, $MgCO_3$, TiO_2, SiC, ZnO_2 etc. Corundum ($\alpha - Al_2O_3$) in an impure form, contaminated with iron oxide and silica, is called *emery* which is unaffected by acids and has high melting point of over $2000^{o}C$.

Classification of Refractories

Based on the chemical behaviour of the refractory constituents, they are broadly classified into three main groups as :

(i) **Acid Refractories**

The acid refractories are acid resistant but are affected by the basic materials. The acid refractories are corundum ($\alpha - Al_2O_3$), iron oxide (FeO), and silica (SiO_2). The acid refractories are very high heat resistant and used to make containers for high temperature reactions.

(ii) **Basic Refractories**

CaO, MgO, $MgCO_3$ etc. are the basic refractories and are unaffected by basic materials but easily attacked by acidic materials. These refractories have low softening point and these materials are used outside the furnace activities.

(iii) **Neutral Refractories**

These refractories consist of weak acid or weak base materials. For example, SiC, FeO, ZrO_2, Cr_2O_3 etc. These refractories are resistant to acid and alkali actions. The important members of the group are graphite, chromite, zirconia, carborundom etc.

8.6.1 Manufacture of Refractories

Different raw materials are used for manufacture of different refractories. The following steps are followed in the manufacture of refractories.

Preparation of Mixture

The raw materials are crushed into a uniform size, about 25 mm, which are further grinded by grinding machine into the size of 200 mesh. The undesirable materials are removed from raw materials by either of the screening process (i) setting, (ii) magnetic separation, and (iii) chemical methods. The screened materials are mixed thoroughly to get proper distribution of plastic materials. Then it is subjected for moulding.

Moulding

Moulding is carried out mechanically or manually under high pressure. Mechanical moulding produces refractories of good strength and high density (low porosity) while the refractories of low strength and low density (high porosity) are obtained from hand moulding process.

Drying

In this method, the moisture from the refractories is removed by using hot air slowly and for a longer period to get good quality desirable refractory.

Firing

The dried refractories are heated under high temperature range of 1400^oC to 1900^oC in a funnel kilns, or shaft kilns or rotary kilns to get high strength, high density, heat and chemical resistant materials.

8.6.2 Characteristics of Refractories

The important characteristics of refractories are outlined below.

(i) They should have high heat resistance (at least 650^oC).

(ii) They should have high reistance to abrasive and corrosive action of flames, molten metals, slags, flue of gases etc.

(iii) They should have high chemical resistance to corrosive action.

(iv) They should expand and contract uniformly with the change of temperature.

(v) They should not suffer any cracks, loss in size and any deformation at the operating temperature.

8.6.3 Properties of Refractories

The following important properties of refractories are as under :

(i) **Refractoriness**

Refractoriness refers to the characteristic of materials which can withstand high temperature at least 600^{o}C without melting or suffering appreciable deformation of shape under the working conditions. Thus, the melting point or softening temperature is the measurement of the refractoriness. The greater the softening temperature or melting point, the better is the refractory. The refractoriness is measured by using pyrometric cones test.

(ii) **Dimensional Stability**

Dimensional stability is the resistance of that material to any change in volume when it is exposed to high temperature for a longer period. Dimension change may be permanent or irreversible or reversible. The more the dimensional stability, the better is the refractory. In irreversible dimensional change, a high degree of vitrification and shrinkage of volume occurs due to the presence of various mixtures of low fusible metallic oxides, e.g. magnesite brick (amorphous MgO) to periclase (denser brick). In case of reversible dimensional change, there is no vitrification and shrinkage.

(iii) **Thermal Expansion**

The better quality of refractory should have low thermal expansion, so that durability and capacity of refractory will increase.

(iv) **Strength of Refractory**

Good refractory possesses high mechanical strength at the normal as well as at operating temperature. Based on strength, the refractories can be grouped into three types as follows :

Under a load of 3.5 kg km^2

(a) A high heat-duty brick should not deform at least below 1350^{o}C. The 10% maximum deformation is permissible.

(b) A medium heat-duty brick should not deform at least below 1300^{o}C (10% maximum deformation is permissible).

(c) Low heat-duty brick should not deform at least below 1300^{o}C (any deformation is not permissible).

(v) **Texture**

High textured (coarse) bricks are more susceptible to the action of abrasion and corrosion because of their large porosity. Dense texured (fine) bricks are resistant to the action of abrasion and corrosion.

(vi) **Porosity**

Porosity refers to the ratio of its pore volume to the blank volume.

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

where, P = Porosity,

W = Saturated weight of specimen,

D = Dry weight of specimen, and

A = Saturated weight + Moisture content in specimen.

(a) With increase in porosity, the strength, resistance to abrasion/corrosion decreases while resistance to sudden change of temperature increases.

(b) With low porosity, the thermal, electrical conductivity and resistance to abrasion/corrosion increases, but resistance to sudden change in temperature decreases.

(vii) **Permeability**

It is the rate of diffusion of gases, liquids, and molten solids through a refractory which depends on size, number of pores, temperature, pressure of the refractory. Permeability is directly related to temperature and inversely to the density.

(viii) **Resistance to Abrasion or Corrosion**

Good refractories have high resistance to abrasion and corrosion.

(ix) **Chemical Inertness**

Acid and base refractories are affected by alkalis and acids, respectively while neutral refractories are inert to both acids and alkalis.

(x) **Thermal Conductivity**

Higher the porosity, lower is the thermal conductivity. Porosity may be increased by burning carbonaceous material to prepare insulating refractory.

(xi) **Thermal Spalling**

It is the property of a refractory that at sudden change in temperature, the refractory breaks, cracks, peels off or develops fracture in it. The bricks of high porosity, good thermal conductivity and low coefficient expansion have low thermal spalling.

(xii) **Heat Capacity**

It is the heat required to raise the temperature by 10^{o}C of the certain volume of refractory. The low porosity and denser refractories have better heat capacity.

(xiii) **Electrical Conductivity**

The electrical resistance of refractories is inversely related to the temperature. Flight-heat duty, high porosity, less denser, high softening temperature, and low thermal expansion refractories have low electrical conductivity.

SAQ 5

(a) What is meant by thermal spalling?

(b) How are refractory materials classified?

8.6.4 Common Refractory Bricks

(A) **Silica Bricks**

The silica bricks contain 90 to 95% of SiO_2 and about 2% lime is added during grinding. Water is mixed with them to make a paste and then moulded. It is dried and fired slowly to achieve the temperature range of 1500°C so that one crystalline from (quartzite) is converted reversibly into another crystalline form (cristobalite). Thus, the final silica brick is a mixture of tridymite, cristobalite and a little amount of quartzite.

Properties

(i) The silica bricks undergo a reversible expansion of 15% when reheated i.e. the bricks return to their original shape and size when cooled.

$$\text{Quartzite} \quad \text{Tridymite} \xleftrightarrow{120^{o}C} \text{Cristobalite}$$

Crystalline α-silica β-silica

Sp. gr. = 2.65 (heavy) Sp. gr. = 2.26 (lighter) Sp. gr. = 2.32 (light)

This transformation is the reversible allotropic transformation.

(ii) Silica bricks do not contract as they have low porosity.

(iii) It is yellowish in colour and has the homogeneous texture, so it is free from air holes and moulding defects.

(iv) In the firing process, heating about 1500°C for 12 to 14 hrs is essential to convert the quartzite to crystobalite otherwise the brick will expand by 17.2% during the use in furnace and cause damage to the structure.

(v) Silica bricks have good load bearing capacity at high temperature (1500 to 1600°C).

(vi) They possess low permeability strength, rigidity and are comparatively light.

(vii) They have high thermal conductivity.

Uses

The main applications of silica bricks are in open hearth steel making furnaces, coke oven walls, roofs of electric furnaces, glass furnaces etc.

(B) **High Alumina Bricks**

They contain 50% alumina or more than that and are obtained by mixing calcined bauxite (Al_2O_3) with clay to make them of less spalling tendency.

Properties

(i) They have high porosity, low thermal conductivity, and low thermal spalling tendency.

(ii) They possess very low coefficient of expansion, high mechanical strength, great resistant to water, gases, solid moltens.

(iii) They have temperature load bearing capacity, excellent chemical stability (Redox conditions).

(C) **Fireclay Bricks**

It is produced from finely ground soft plastic material fireclay, $Al_2O_3.2SiO_2.2H_2O$ in which silica content is high about 50 to 55%, and the other approximate composition is 40 to 50% Al_2O_3 and the balance is metallic oxides like K_2O, FeO, CaO, MgO, CrO_2 etc. This composition may be slightly changed depending on the nature (acid, basic or neutral) of bricks. To this composition, powdered calcined fireclay is mixed to make it thermal spalling resistant.

Properties

(i) Fire clay are light yellow to reddish brown in colour depending the contents of iron oxide percentage.

(ii) Due to high percentage of SiO_2, fire clay is acidic in nature, so it is not attacked by acids, but can be attacked by alkalies.

(iii) They possess low porosity and low refractoriness character.

(iv) The load bearing capacity is generally lower and it fuses at about 1400^oC.

(v) It has better thermal spalling resistance and have very high crushing strength.

(vi) They can be subjected to sudden change of temperature without melting or deforming of the shape.

Uses

These are generally used as refractory bricks, and are used for construction of blast furnaces, crucible furnaces flues, kilns, boiler setting etc.

(D) **Magnesite Bricks**

This brick is obtained by mixing of caustic magnesia or sulphite or iron oxide as binding material to a properly powdered calcined magnesite (MgO). Then it is made into a paste with water to subject for moulding into bricks. Then it is dried and fired slowly up to 1500^oC for about 8 to 10 hrs. and then allowed to cool it to get the final brick.

Properties

(i) It is basic in nature so it is easily attacked by acids not by the alkalies.

(ii) Since it has very high melting point (2800^oC), it can be used upto 2200^oC to 2400^oC without load and upto 1500 to 1700^oC with loading capacity of 3.5 kg/cm^2.

(iii) It has good mechanical strength and has little shrinkage effect.

(iv) It is sparingly soluble in water giving an alkaline reaction, and when heated with carbon, magnesium carbide is formed which is less abrasion resistant.

Uses

Magnesite bricks are employed for lining basic steel and other metallurgical furnaces, crucibles, antimony ores.

(E) **Chromite Bricks**

These bricks are obtained by crushing the chromites with binding material (FeO_2), (CrO_3) and then moulded and fired at 1500 to 1700^oC to get final bricks.

Properties

(i) These are dark green in colour and are not attacked by water or acids.

(ii) They possess high density, so low thermal conductivity.

(iii) Low thermal spalling resistantce and can be used upto 1400^oC with loading capacity of 3.5 kg/cm^2.

(iv) They have good crushing strength.

Uses

Since they are not attacked by water or acids, they may be applied in separating acidic and basic refractory lining at high temperature. Thus, it prevents the acid base interaction.

(F) **Chorme-magnesite Bricks**

This is obtained by blending chrome ore with magnesite, then it is moulded manually or mechanically and subjected to firing. During firing, the serpentine $3MgO.2SiO_2.H_2O$ present in the chrome ore decomposes to yield forsterite $2MgO.SiO_2$ and magnesite silicate, $MgSiO_3$. The latter then combines with MgO to form forsterite as follows :

$$\underset{\text{Serpentine}}{3MgO.2SiO_2.H_2O} \xrightarrow{\Delta} \underset{\text{Forsterite}}{2MgO.SiO_2} + MgSiO_3 + H_2O$$

$$MgSiO_3 + MgO \rightarrow 2MgO.SiO_2 \text{ (Forsterite)}$$

Chrome-magnesite bricks are of two types depending on higher percentage of respective ore. For example, if chrome ore percentage is more about 25 to 40% and MgO (40-50%), then it is said to be chrome-magnesite refractories.

If the magnesite percentage is high, i.e. about 55% to 68% and 8 to 15% chrome ore then it is said to be magnesite-chrome refractories.

Sl. No.	Magnesite-chrome Refractories	Chrome-magnesite Refractories
1	Higher refractories (about 2300^oC)	Comparatively low refractoriness (about 1800 to 1900^oC)
2	Higher thermal spalling resistance	More prone to thermal spalling

3	Higher thermal conductivity	Low thermal conductivity
4	High abrasion and corrosion resistant to gases, slags and molten solids	Less resistant to abrasion/corrosion actions.

(G) Dolomite Bricks

Dolomite bricks are generally obtained by mixing the silicate binder with equimolecular proportion of CaO and MgO which is then subjected to firing at about 1500°C for a period of 24 hrs. to produce the stabilised final bricks.

Properties

(i) It is amorphous refractory with less strength and high porosity.

(ii) It is hygroscopic in nature and is more soft.

(iii) They are poor resistant to thermal shocks and having greater shrinkage property.

(iv) It is an insulator to electricity and heat.

(v) But these bricks have good load bearings capacity, i.e. 3.5 kg/cm^2 at 1600°C.

(vi) It is basic in nature, so more resistant to alkali but attacked by acids.

(vii) When serpentine ($MgO.SiO_2$) is blended with this, quality of the bricks changes as di and tri calcium silicate is produced which is in many ways resistant to water and gases (CO_2).

(viii) It is having good chemical stability.

Uses

These are generally used for basic electric furnace lining, open hearth furnaces, ladle linings etc. and the furnaces where basic products are processed. This can also be used as substitute for magnesite bricks.

(H) Carbon Bricks

Coke is finely crushed with graphite or pitch or tar and then ground with clay thoroughly. Now it is moulded and introduced to furnace for firing at about 1300-1400°C to obtain carbon bricks. During the firing, sand blasting or powdered coke blasting is necessary to make the carbon bricks dense and comparatively less porous.

Properties

(i) Carbon bricks are very prone to the oxidation reaction in air at elevated temperature, therefore they are useful under reduction and neutral conditions.

(ii) They are infusible and resistant to thermal spalling.

(iii) They have close texture, so high thermal conductivity.

(iv) They are resistant to chemicals (acid, alkali and other solvents).

(v) They can withstand sudden changes of temperature without deformation of shape.

Uses

Carbon refractories can be used in lining of highly chemically resistant equipments, electric furnace, and in coper, aluminium and lead smelting furnaces. They are also used in construction of electrodes, atomic reactors etc.

(I) **Carborundom (SiC) Bricks**

A mixture of sand (54%), coke (34%), saw dust (10%) and small amount of salt (2%) is heated in an electric furnace at 1550°C to 2000°C by passing acetylene on heated silicon. The following reaction occurs resulting in the formation of SiC under this operation temperature.

$$SiO_2 + 3C \rightarrow SiC + 2CO \uparrow$$

$$2Si + C_2H_2 \rightarrow 2SiC + H_2 \uparrow$$

During this process, saw dust and salt are used to increase the porosity of the article. At the end of the operation, the dark colored mass of black crystals of SiC is crushed with H_2SO_4 and NaOH solution to remove the impurities. It is finally dried in kilns and graded into various portions according to the size of the particles.

Properties

It is colorless when pure. It is very hard, clay bonded silicon carbide bricks can be used upto 1800°C and it does not decompose below 2200°C. Chemically, it is extremely inert and even at high temperature, it is not attacked by HF, HCl, O_2 or S. Silicon nitride bonded bricks have a high strength, good resistant thermal shock than clay bonded ores. These have high density, high abrasion resistant, good mechanical strength, low thermal expansion and good thermal conductivity. SiC exists in three forms which are related to one another as diamond, zinc blende and wurtzite.

Uses

Due to its high electrical and heat conductivity, it is used for making crucibles, as carbon rods in resistant heaters, furnaces etc. It is used in furnace lining and as an abrasive for cutting and grinding glasses. It is also used as deoxidant in metallurgy and as resister for electrical furnaces.

(J) **Beryllia (BeO) Bricks**

The finely powdered beryl ($2BeO.Al_2O_3.6SiO_2$) is fused with potassium carbonate at about 1500°C to 1900°C in an electrical furnace and then evaporated with conc. H_2SO_4. The resulting mass is extracted with boiled water and filtered to get BeO bricks.

Properties

It is silvery white in color, malleable and possesses a high melting point (2550°C). It has good resistant to thermal shocks, CO_2, CO, and water. It has high thermal conductivity and low resistant to acids and alkalis.

Uses

It is used as a moderator in nuclear reactors as it absorbs fewer neutrons and it finds place in the fields of developing rockets, missiles and high speed air crafts. It is also used for making electrodes of neon signs, windows and X-rays tubes, etc. But beryllia dust is very hazardous to health even in small quantity.

(K) Zirconia Bricks

These are obtained by heating zirconia mineral (ZnO_2) and colloidal zirconia or alumina in an electrical furnace at about 1700^{o}C to 1800^{o}C. MgO or CaO may be added as stabilizer during the heating process to avoid volume changes on heating and cooling.

Properties

These are neutral refractories. They have high load bearing capacity, i.e. 3.5 kg/cm^2 at about 1900^{o}C but they can be used upto 2600^{o}C without loading. They are resistant to thermal shocks.

Uses

These are used in high frequency electric furnaces and other furnaces where very high temperature is maintained.

Table 8.1 : Properties of Common Refractories

	Refractory	Major Component (% by wt.)	Refractoriness (^{o}C)	Porosity (%)	Thermal Resistance	Abrasion Resistance	Acidic Slags & Fluxes	Basic Slags & Fluxes
1		SiO_2 = 93-96	1700	16-18	Good (1600^{o}C)	Good	Fair	Poor
2		SiO_2 = 40-45 Al_2O_3 = 35-55	1700	20-23	Good	Good	Good	Medium
3	High alumina	Al_2O_3 = 50-60 SiO_2 = 40-45	1750	20-29	Good	Good	Good	Poor
4	Magnesite	MgO = 80-95 Fe_2O_3 = 2-7 Al_2O_3 = < 4	< 2000	20-23	Poor	Medium	Poor	Good
5	Dolomite	CaO = 58 MgO = 40	1650	= 20	Poor	Medium	Poor	Good
6	Carbon	C = 85-90	< 2000	22-32	Good	Poor	Good	Fair
7	Chromite	Al_2O_3 = 15-23 Cr_2O_3 = 30-15 Fe_2O_3 = 10-17 MgO = 14-20	1800 – 1900	18-25	Fair	Medium	Fair	Good
8	Carborundum	SiC = 89-91	< 2000	17-20	Good	Good	Good	Poor
9	Zirconia	ZrO_2 = 67	= 2500	—	Good	Good	Good	Poor
10	Beryllia	BeO = 99	= 2500	= 30	Good	—	Poor	Good

(L) Cermets

It is the material having characteristics of ceramics and metals. It is basically a hot pressed to sintered material. Generally, the cermets contain about 80% of ceramic materials (highly refractory carbides, oxides, borides, silicates and sulphides, carbides of zirconium, molybdenum, tungsten, titanium, chromium etc.) the oxides of magnesium aluminium etc., and the borides of zirconium, tungsten etc. and 20% of the metal iron, aluminium, chromium, cobalt, nickel, molybdenum etc. are used.

Properties

(i) They have high refractories of ceramics.

(ii) High thermal conductivity of metals.

(iii) High thermal shock resistance of metals and high shapeability.

Uses

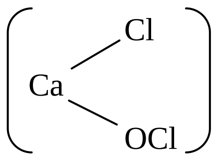
These are generally used as highly refractories in rocket, jet engine parts, spinning tools for hot metals, hot forging dies, and in the fields where high temperature, high shock resistance are required.

SAQ 6

Explain the different steps involved in the manufacture of silica bricks.

8.7 BLEACHING POWDER

Bleaching powder is a mixed salt of hydrochloric acid (HCl) and hypochlorous acid (HClO). The molecular formula of bleaching powder is $CaOCl_2$ or Ca(OCl)Cl. The structural formula is as follows:



$\rightarrow$ Bleaching Powder

Thus, bleaching powder is calcium chloro-hypochlorite.

8.7.1 Manufacture

Bleaching powder is manufactured by the interaction of chlorine and dry slaked lime, $Ca(OH)_2$. In the manufacturing process, the temperature should be maintained below $40^{o}C$ and chlorine (Cl_2) in dilute condition should be used. In this method, there are two views regarding the formation of bleaching powder as follows :

(i) Olding's View (1861)

This view satisfies the molecular formula of bleaching powder as Ca(OCl)Cl.

$$Ca(OH)_2 + 2Cl_2 \rightarrow \underset{\text{Bleaching Powder}}{Ca(OCl)Cl} + H_2O$$

(ii) Bunn, Clark and Clifford's View (1935)

It satisfies the formula $CaOCl_2$.

$$2\,Ca(OH)_2 + 2\,Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + H_2O$$

$$CaCl_2 + Ca(OH)_2 + H_2O \rightarrow CaCl_2.Ca(OH)_2.H_2O$$

$$3\,Ca(OH)_2 + 2\,Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2.Ca\,(OH)_2 + H_2O$$

Bachmann's plant is the most modern method for manufacture of bleaching powder.

8.7.2 Bachmann's Plant

The main components of the plant are (i) iron tower and (ii) shelves, and rotating rakes. Depending on the production capacity, iron tower is fitted with eight to ten shelves at fixed height and each is equipped with rotating rakes (Figure 8.3). Slaked lime is introduced into the tower at the top through a hopper. Chlorine and hot air are introduced at the bottom of the tower to produce a counter current. Slaked lime comes downward with the help of rotating rakes whereas Cl_2 moves upward. Thus, they interact with each other and form bleaching powder which is collected at the bottom of the tower. There is an outlet at the top of tower for undesired air and chlorine.

Figure 8.3 : Bachmann's Plant for Bleaching Powder Manufacture

8.7.3 Properties

Physical

(i) It is a yellowish white solid.

(ii) It strongly smells of chlorine.

(iii) It is soluble in water.

Chemical

(i) It decomposes with water.

$$2\,CaOCl_2 + H_2O \rightarrow CaCl_2 + Ca(OCl)_2 + H_2O$$

$$Ca(OCl)_2 \rightarrow CaCl_2 + H_2O$$

(ii) It undergoes auto oxidation on standing.

$$6\,CaOCl \rightarrow Ca(ClO_3)_2 + 5\,CaCl_2$$

In presence of catalyst $CoCl_2$, it loses its oxygen

$$6\,CaOCl_2 \xrightarrow{CoCl_2} 2\,CaCl_2 + O_2$$

(iii) It releases Cl_2 with excess dilute acids.

$$CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$$

$$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$$

It produces nascent oxygen with less quantity of dil. acids.

$$2\,CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + CaCl_2 + 2\,HCl + 2\,O$$

(iv) Bleaching and oxidizing action: It acts both as an oxidizing and bleaching agent. Oxidizing action is due to the production of nascent oxygen. Bleaching action is due to nascent oxygen and chlorine.

$$\left.\begin{array}{l} PbO + CaOCl_2 \rightarrow PbO_2 + CaCl_2 \\ MnO + CaOCl_2 \rightarrow MnO_2 + CaCl_2 \end{array}\right\} \text{Oxidation}$$

In presence of CH_3COOH

$$CaOCl_2 + 2\,KI + 2\,CH_3COOH \rightarrow (CH_3COO)_2\,Ca + 2\,KCl + H_2O + I_2$$

Bleaching action

(v) It reacts with alcohol and ketone.

(a) $4\,CaOCl_2 + 2\,C_2H_5OH \rightarrow 2\,CHCl_3 + (HCOO)_2\,Ca + Ca(OH)_2 + 2\,H_2O + CaCl_2$

(b) $3\,CaOCl_2 + 2\,CH_3COCH_3 \rightarrow \underset{\text{chloroform}}{2\,CHCl_3} + (CH_3COO)_2\,Ca + 2\,Ca(OH)_2 + 2\,H_2O$

(vi) It reacts with ammonia solution to liberate N_2 gas.

$$3\,CaOCl_2 + 2\,NH_4OH \rightarrow CaCl_2 + 5\,H_2O + N_2$$

8.7.4 Uses

(i) It is used as a disinfectant and germicide for drains and other stagnant waters.

(ii) It is used for bleaching cotton, linen, wood, straw, silk, textile etc.

(iii) It is used for sterilization of water.

(iv) It is used for manufacture of chloroform.

(v) It is used as an oxidizing agent in industries.

(vi) It is used for making wool unshrinkable.

(vii) During war time, it is used to remove the poisonous gases from atmosphere.

8.8 COMMERCIAL BLEACHING POWDER

The commercial bleaching powder is evaluated from its available chlorine (35-40%). The actual percentage of available chlorine is 49%.

Estimation of Available Chlorine

$$\underset{40+16+71+18=145}{CaOCl_2.H_2O} + H_2SO_4 \rightarrow CaSO_4 + 2\,H_2O + \underset{71}{Cl_2}$$

145 g of $CaOCl_2.H_2O$ contains = 71 g. Chlorine

1 g of $CaOCl_2.H_2O$ contains = $\frac{71}{145}$ g

100 g of $CaOCl_2.H_2O$ contains = $\frac{71}{145} \times 100\text{g} = 49\%$

The low percentage of chlorine in commercial bleaching powder is due to loss of chlorine to atmosphere and impurities and incomplete reaction between slaked lime and chlorine during manufacture.

Iodometric Method

In this method, an excess of potassium iodide and acetic acid is added to the aqueous solution of bleaching powder which will liberate I_2. This liberated iodine is titrated against standard solution (N/10) of sodium thiosulphate using starch as an indicator.

Reactions involved are :

$CaOCl_2 + 2\ CH_3COOH + 2\ KI \rightarrow (CH_3COO)_2Ca + 2\ KCl + H_2O + I_2$

$2\ Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\ NaI$

1 ml. of N/10 $Na_2S_2O_3 \equiv$ 0.00355 g. of available chlorine.

SAQ 7

(a) What is available chlorine?

(b) How would you obtain bleaching powder from slaked lime?

(c) How will you determine the actual available chlorine in bleaching powder?

(d) Explain the formation of chloroform from bleaching powder.

8.9 SUMMARY

In this unit, you have learnt that

- Glass formation is the solidification of the liquid state without crystallization.
- Glass does not have a sharp melting point.
- Glass transition is the frozen state of the disordered structure of the liquid without change of its order.
- Cerium oxide absorbs ultraviolet light, thus it is used in optical glass.
- Annealing avoids any cracking of glass articles.
- Glaze is a glossy coating over pottery to make the article impervious to liquid.
- The minimum temperature at which a solid begins to soften and loses its shape and size.
- Refractories are able to withstand high temperature without appreciable deformation in shape.
- Cermets are hot pressed materials consisting of combination of ceramics and metals.

- Porosity varies inversely with thermal conductivity.
- Neutral refractories are resistant to both acids and alkalis.
- Bleaching powder serves as both bleaching and oxidizing agent.

8.10 ANSWERS TO SAQs

SAQ 1

(a) It is amorphous transparent solid produced by solidifying the liquid state.

Borax lowers the coefficient of expansion and increases the durability of glass. Alumina makes glass resistant to sudden changes of temperature.

(b) (ii)

SAQ 2

(a) Because thay have open structures which generally have low heat of fusion.

(b) The temperature at which the rate of change of viscosity is highest.

(c) Surface treatment and compressive stress methods.

SAQ 3

Because it contains cerium oxide which prevents UV light.

SAQ 4

(a) Refer to Sub-section 8.5.3.

(b) They are engineering materials which can be used at high temperatures. They can be classified as clay products, glasses and refractories.

(c) It means the ability of the clay to form a plastic mass with water for moulding purposes.

SAQ 5

(a) It is the property of a refractory which makes it break, crack, peal off or develop fracture in it on sudden temperature change.

(b) Acid, basic and neutral refractories.

SAQ 6

Refer to Sub-section 8.6.4.

FURTHER READING

Balram Pani (2001), "*A Textbook on Engineering Chemistry*", Galgotia Publications Pvt. Ltd.

S. S. Kumar, S. K. Mahajan and A. S. Khatri (2001), "*Applied Chemistry*", 6th Edition, H. Tata Publication.

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CHEMISTRY

Today we live in a world of materials. We come across a large variety of man-made and naturally occurring substances. In fact, man has found out ways to use naturally occurring materials and design and develop new material to meet the requirements of modern living. The study of structure, properties and uses of these materials forms a part of the branch of science called Chemistry. In this material, we have tried to expose you to various types of naturally occurring elements which can be classified as non-metals or metals. Water, which is no way less important than any other substance, has also been dealt with. The latter half of the course material gives you an idea about various materials used in daily life to make our living comfortable. These include fuels, lubricants, polymers, glass and ceramics.

The course has been divided into eight units.

Unit 1 deals with the periodic table and explains how different elements can be grouped according to their properties. It also covers periodic properties such as valence, atomic and ionic radii and metallic character etc. and their variation for different elements.

Unit 2 involves the study of common non-metallic elements such as hydrogen, oxygen and ammonia, chlorine and acids. It discusses their occurrence, properties and importance.

Unit 3 covers metals such as iron, copper and aluminium. These metals have been in use by mankind since ancient times. Alloys which are made to further modify the properties of metals are also discussed in this unit.

Unit 4 is about Water Technology. It covers the sources, structure and importance of water. Water is needed for domestic, industrial and agricultural uses. Hardness and pH of water greatly affect its above uses. Here, we have explained how hard water can be treated to make it fit for use. Under industrial uses, water used in boilers leads to the formation of scales and sludges and boiler corrosion. You will study about these aspects and also water treatment in detail in this unit.

Unit 5 deals with Fuels. This unit highlights the importance of various solid, liquid and gaseous fuels. It gives you an idea about the different fuels, their relative advantages, composition and important uses.

Unit 6 discusses lubricants which are used to minimize friction and wear and tear of moving machine parts. They have their unique importance in industry. This unit covers how to select a suitable lubricant. In addition to this, the classification of lubricants have been discussed along with their characteristic properties.

Unit 7 deals with polymers which are the materials of 21st century. Today, no such area of study or application is there, where polymers are not used in one way or the other. In this unit, we have discussed various types of polymers, their properties and applications. You will study about polymer, nylon, rubber, plastic etc. in this unit.

The last unit, i.e. Unit 8, is about Glass and Ceramics. It highlights the manufacture of glass and also discusses various varieties of glass and their uses. Ceramics and particularly refractories have also been explained in detail because of their importance as engineering materials. Finally, manufacture, properties and commercial use of bleaching powder have been dealt.

We hope that such a wide variety of materials would definitely excite you about them and their importance. So whenever you look around you, try to find which materials constitute various objects in your surrounding. We hope you would be better able to appreciate their unique uses and importance after studying this course material.

1.8 TERMINAL QUESTIONS

(i) What is a Triad?

(ii) State the NewLand's Law of Octaves.

(iii) What is Modern Periodic Law?

(iv) Give the contributions of Mendeleev in the classification of elements.

(v) What are periodic properties? Name three periodic properties.

(vi) Define valence. How does it vary across a period in the periodic table?

(vii) Explain the variation of atomic radii down a group and across a period in the periodic table.

(viii) Give reason why a cation is smaller than its parent atom.

(ix) Define ionization energy. Why is the second ionization energy higher than the first?

4.13 ANSWERS TO TERMINAL QUESTIONS

SAQ 1

What are scales? What are bad effects of scales?

Distinguish between softening and demineralization of water.

How can scale formation be prevented by calgon conditioning? Describe.

SAQ 2

(a) Name the different methods of desalination. Explain any one of them.

(b) What are zeolites? How do they function in removing the hardness of water?

(c) What are the types of hardness of water?

SAQ 3

(a) Describe phosphate conditioning of boiler water.

(b) Explain caustic embritterment and its prevention.

(c) Describe the various anomalous behaviour of water.

SAQ 4

(a) Give the structure of water.

(b) Why water is a better solvent than any other solvent.

(c) Explain priming and foaming.

SAQ 5

Explain the followings :

(i) Reverse Osmosis.

(ii) Sterilization of water.

(iii) Ion exchange resins.

6.10 TERMINAL QUESTIONS

(i) Define lubricants. Give classification of lubricants with suitable examples.

(ii) Define lubrication. Explain the fluid film and boundary film lubrication.

(iii) Discuss the selection of a lubricant.

(iv) What are the solid lubricants? Discuss their uses.

(v) In case of a liquid lubricant

- (a) flash and fire points are identical.
- (b) fire point is lower than the flash point.
- (c) flash point is higher than the fire point.
- (d) fire point is higher than the flash point.

(vi) What is grease?

(vii) Define viscosity and viscosity index of an oil. How is the viscosity of an oil determined with Redwood viscometer No.1?

(viii) What is the importance of fire point of lubricant?

(ix) A good lubricant possesses

- (a) high volatility
- (b) low fire point
- (c) low viscosity index
- (d) high viscosity index

(x) What do you understand by flash point and fire point? Describe the method of their determination using Pensky Marten's apparatus.

(xi) Briefly explain the following for lubricants.

(xii) Write in brief in regard of lubricants

- (a) cloud and pour point
- (b) corrosion stability
- (c) oxidation stability
- (d) oiliness

(xiii) (a) Fatty acids are no longer used as lubricants, why?

- (b) Lubricants are purposely placed between two solid surfaces. Explain in detail.

(xiii) Illustrate the significance of following parameters of an oil with regard to lubricants.

- (a) Viscosity
- (b) Flash and Fire point
- (c) Cloud and Pour Point
- (d) Oxidation stability.

8.11 TERMINAL QUESTIONS

(i) Write short notes on :

(d) Pyrex glass

(e) Flint glass

(f) Crooke's glass

(g) Jena glass

(h) Borosilicate glass.

(ii) What is the significance of acidic, basic and neutral refractories?

(iii) Write short notes on

(a) Magnesite bricks,

(b) Carbon bricks, and

(c) Fireclay bricks.

(iv) What are the functions of various ingredients used in the manufacture of glass?

(v) What is meant by whitewares? Give their two uses.

(vi) Explain the followings :

(a) The liquid glazing of ceramics.

(b) Refractories under load thermal spalling and porosity of refractories.

(vii) What are the significance of acidic, basic and neutral refractories? Explain with examples.

(viii) How would you obtain bleaching powder from slaked lime.

(ix) How is bullet proof glass is prepared?

(x) What is the purpose of annealing of glass?

(xi) Why do we add a little cerium oxide to optical glass?

(xii) Give reason for the oxidizing action of bleaching powder.

(xiii) How would you calculate the available chlorine in bleaching powder?

(xiv) How are refractory materials classified?

(xv) What is fracture? How would you prevent brittle fracture in glass?

(xvi) What is glass transition temperature? Give its importance.