UNIT-3: ENGINEERING MATERIALS-1

Q1. Write a brief account on composition and classification of cement.

Cement: Concrete is most widely used non-metallic material in construction of buildings, dams, bridges, high ways etc. In concrete, cement is the essential bonding material which binds sand and rock when mixed with water.

Cement is a dirty greenish heavy powder and finds its importance as a building material. It can be described as material possessing adhesive and cohesive properties and capable of bonding materials like stones, bricks, building blocks etc. Cement has the property of setting and hardening in the presence of water. So it is called as hydraulic cement. The essential constituents of cement used for constructional purposes are compounds of calcium (calcareous) and Al +Si (argillaceous).

Classification: - Cement is classified into four types, based on the chemical composition.

1. Natural cement
2. Puzzolona cement
3. Slag cement
4. Portland cement

Of these, Portland cement is the most widely used cement.

Portland cement: It is most widely used non-metallic material of construction. It is a mixture of calcium silicates and calcium aluminates with small amount of gypsum.

The name Portland cement is used because this powder on mixing with water gives a hard, stone like mass which resembles Portland rock.

Properties:-All Portland cements are hydraulic in nature

Composition of Portland cement:-

A good sample of Portland cement

- Calcium Oxide or lime (CaO) : 60-70%
- Silica (SiO_2) : 20-24%
- Alumina (Al_2O_3) : 5-7.5%
- Magnesia (MgO) : 2-3%
- Ferric Oxide (Fe_2O_3) : 1-2.5%
- Sulphur trioxide (SO_3) : 1-1.5%
- Sulphur Oxide (Na_2O) : 1%
- Potassium Oxide (K_2O) : 1%

Q2. Write a brief account on setting and hardening of cement.

Setting and Hardening of cement:-

Cement when mixed with water forms a plastic mass called cement paste. During hydration reaction, gel and crystalline products are formed.

The inter-locking of the crystals binds the inert particles of the aggregates into a compact rock like material.

This process of solidification comprises of

(i) setting and then

(ii) hardening

Setting is defined as stiffening of the original plastic mass due to initial gel formation. Hardening is development of strength, due to crystallisation.

Due to the gradual progress of crystallisation in the interior mass of cement, hardening starts after setting. The strength developed by cement paste at any time depends upon the amount of gel formed and the extent of crystallisation. The setting and hardening of cement is due to the formation of inter locking crystals reinforced by rigid gels formed by the hydration and hydrolysis of the constitutional compounds.

Reactions involved in setting and hardening of cement:-

When cement is mixed with water, the paste becomes rigid within a short time which is known as initial setting. This is due to the hydration of tricalcium aluminate and gel formation of tetra calcium alumino ferrite.

$$3\,CaO.Al_2O_3 + 6\,H_2O \longrightarrow 3\,CaO.Al_2O_3.6\,H_2O + 880\text{ KJ/Kg}$$

$$C_3A \quad + \quad 6\,H_2O \longrightarrow C_3A.\,6\,H_2O + 880\text{ KJ/Kg}$$

tricalcium aluminate — hydrated tricalcium aluminate (crystalline)

$$4\,CaO.Al_2O_3.Fe_2O_3 + 7\,H_2O \longrightarrow 3\,CaO.Al_2O_3.6\,H_2O + Cao.Fe_2O_3.H_2O + 420\text{ KJ/Kg}$$

$$C_4AF \quad + \quad 7\,H_2O \longrightarrow C_3A.\,6\,H_2O \;+ CF.H_2O + 420\text{ KJ/Kg}$$

tetracalcium alumino ferrite — (crystalline) gel

Dicalcium silicate also hydrolyses to tobermonite gel which contributes to initial setting.

$$2(2\,CaO.SiO_2) + 4\,H_2O \longrightarrow 3\,CaO.2SiO_2.6H_2O + Ca(OH)_2 + 250\text{ KJ/Kg}$$

$$2\,C_2S \quad + \quad 4\,H_2O \longrightarrow C_3S_2.6H_2O \;+\; Ca(OH)_2 + 250\text{ KJ/Kg}$$

Dicalcium silicate — tobermonite gel

Final setting and hardening of cement paste is due to the formation of tobermonite gel and crystallisation of calcium hydroxide and hydrated tricalcium aluminate.

$$2(2\ CaO.SiO_2) + 6\ H_2O \longrightarrow 3\ CaO.2SiO_2.3H_2O + 3Ca(OH)_2 + 500\ KJ/Kg$$

$$2\ C_3S \quad + \quad 6\ H_2O \longrightarrow C_3S_2.6H_2O \quad + \quad 3Ca(OH)_2 + 500\ KJ/Kg$$

tricalcium silicate — tobermonite gel — calcium hydroxide (crystalline)

During setting and hardening of cement, some amount of heat is liberated due to hydration and hydrolysis reactions. The quantity of heat evolved during

Complete hydration of cement is 500 KJ/Kg.

Sequence of chemical reactions during setting & hardening:-

Cement + Water paste	1 day ------------>	hydration of C_3A and C_4AF	7 days ----------->	gelation of C_3S	28 days ------------->	gelation of C_2S & C_3S

Function of gypsum in cement:-

Tri calcium aluminate (C_3A) combines with water very rapidly.

$$C_3A + 6H_2O \longrightarrow C_3A\ .\ 6H_2O + heat$$

After the initial setting, the paste becomes soft and the added gypsum retards the dissolution of C_3A by forming insoluble calcium sulpho aluminate.

$$3\ CaO.Al_2O_3.x\ CaSO_4.7\ H_2O$$

This reaction prevents the high concentration of alumina in the cement solution and hence retards the early initial setting of cement.

Q3. Write a short note on classification, properties and applications of ceramics.

Ceramics:

The word ceramic is obtained from Greek word "keramos" which means burnt stuff. Ceramics are inorganic non-metallic material that are processed and used at high temperatures. They include silicates, metallic oxides and their combination ceramic materials having wide range of properties are produced for different applications.

Ceramics generally consist of three major components:

Plastic portion: this is usually provided by clay, which imparts the necessary plasticity and workability.

A flux or glassy materials: This is provided by (kAlSio8), which helps in bonding and cementing the ingredients together.

A non-plastic refractory crystalline portion: this is provided by silica, which contribute mechanical strength.

Ceramics are mainly classified into three types:

1. Clay products
2. Refractories
3. Glasses according to their characteristic features.

Clay products are divided into three main types:

- Structural clay products which contain iron oxides. They are used for bricks, tiles and similar products.
- Whites wares which are pales substances such as porcelain and chain.
- Chemical stone wares which are specially treated to be hard, and non-porous.

Clay: The term clay denotes certain earths which are highly plastic when wet and when heated to redness, loses their plasticity and are converted into a hard mass which is unaffected by water .

Clay is composed of hydrated aluminium silicates ($Al_2O_3.2SiO_2.2H_2O$) together with other substances such as mica and quartz. Calcined fire clays are called grog primary clay burns white and it is called kaolin or china clay.

Structural clay products*:* they include bricks, tiles, blocks and glazed & unglazed decorative products. Most of the structural clay products are made from relative low grade clays, shales and grog.

White wares or white pottery: the materials that give products which are white or pale-cream in colour after firing. The raw materials used for the manufacture of white ware contain little or no compounds of iron. White wares are made by mixing china clay, feldspar and flint (SiO_2). The proportions of these components are adjusted according to the properties desired in the finished articles.

White wares posses' good strength, translucency and very low porosity. This is attained by firing the products at high temperatures of 1450-1500degrees with partial vitrification.

White ware products consist of refractory body and glassy coating called as glaze. They are made by two main processes.

- Porcelain process in which the glaze and body are developed in one firing process.
- China process in which the glaze is applied in a separate state.

Uses of white wares: they find application as spark-plugs, electrical insulators, laboratory equipment, dishes, high-class potteries etc.

Earthen wares and stone wares: the clay products which are stone like hard, strong and obtained by burning at low temperatures are called earthen wares. They are softer variety which are obtained by burning at high temperatures are called stone wares.

Earthen wares: these are obtained from mixed earth clay or clay mixed with sands, crushed pottery etc. stone wares are made from refractory clays mixed with crushed stone, crushed pottery etc. both types are glazed to made them compact, stronger and impersions to water and most liquids.

Chemical stone wares: chemical stone wares differ white wares in colour and they are coarse and robust. They have low absorption power, high density, physical strength and chemical resistance.

They consist: Ordinary clay -50%
Kaolin-5%
Feldspar-20%
Grog-10%
Flints-15%

They are shaped by moulding or throwing on a potter's wheel or casting. After shaping,the articles are dried and fired at high temperatures of above 1000degrees. They are glazed by salt glazing method in which fired articles are raised to about 1000degrees and common salt is thrown on them.

The vapour of salt produces sodium aluminium silicate which fills the surface pores. This glaze is resistant and makes the articles impermeable to liquids.

Uses of stone ware: they are used for the construction of sanitary fixtures like sinks, bath tubes etc. piping vessels, drainage pipes, underground cable sheathings, sewerage pipes, absorption towers, values, pumps in chemical industry.

Properties of ceramics: the characteristics of ceramic materials are as follow:

- They are usually hard and brittle in nature and generally being in the form of amorphous or glassy solids.
- The atomic bonding in these materials is of mixed ionic or covalent character.
- They have good electrical resistance and act as insulator.
- They have high temperature resistance.
- They have good resistance to chemical attack and weathering.
- They have high compressive strength and textile strength.
- The ceramic materials have lower spalling resistance than metals.
- They are resistance towards corrosion. They have high hardness values. They are brittle in nature. Ceramic materials are good thermal and electrical insulators this is due to the absence of conduction electrons.
- Ceramic materials are polarizable. Some ceramic materials can be highly polarized with electric charge. They are used as dielectric materials for capacitors.

Q4. Define lubricant. Discuss the important properties of a good lubricant and its significance.

In all types of machines, the surfaces of moving or sliding or rolling parts rub against each other. This mutual rubbing of one part over the other leads to resistance of movement which is called as friction.

Friction causes a lot of wear and tear of surfaces of moving parts and since heat generated in this process, it reduces the efficiency of the machinery. The problems of frictional resistance can be minimised by using lubricants which forms a thin layer between the moving parts.

A lubricant is defined as a substance introduced between two moving or sliding surfaces and reduces the frictional resistance between them. This phenomenon of reducing frictional resistance between the two surfaces by the introduction of lubricants in between them is called lubrication.

Criteria of a good lubricant:- A good lubricant must have the following functions.

- The first and foremost function is to reduce friction.
- It reduces surface deformation, wear and tear because the direct contact between the rubbing surfaces is avoided.
- It reduces waste of energy. Hence the efficiency of the machine is enhanced.
- It reduces expansion of metal by local frictional heat.
- It avoids seizure of moving surfaces as the lubricant minimises the liberation of frictional heat.
- It avoids unsmooth relative motion of moving parts.
- It reduces the maintenance and running cost of machine, by preventing rust and corrosion.
- It also acts as a seal.

Q5. Explain the different theories of the mechanism of lubrication.

Mechanism of lubrication:-

There are mainly three types of mechanisms by which lubrication takes place. They are:

(i) Fluid film or thick film or hydrodynamic lubrication

(ii) Boundary lubrication or thin film lubrication

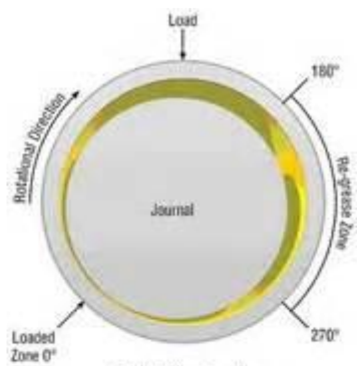
(iii) Extreme pressure lubrication

(i) Fluid film lubrication:-

- In this type of lubrication, the moving or sliding surfaces are separated from each other by a thick film of fluid, so that there is no direct contact between them.

- The lubricant film covers the irregularities of the surfaces and reduces friction and wear and tear.
- The resistance to movement of sliding or moving parts is due to internal resistance between the particles of the lubricant moving over each other.
- For this, the lubricant should have minimum viscosity under working conditions. It should remain in place and separate the surfaces.
- The coefficient of friction which is a ratio of force required to cause motion to the applied load is as low as 0.001 to 0.03.

Delicate instruments, light machines like watches, clocks, guns, sewing machines etc. are provided with fluid film lubrication.



Fluid Film Bearing

The fluid film lubrication is done by hydrocarbon oils. These are blended with selected long chain polymers to maintain the viscosity of oil as constant in all seasons. The viscosity of hydrocarbon oils increases with increasing molecular weight.

Hence appropriate fractions are blended from petroleum refining to meet the requirement for different applications.These fractions contain small quantities of unsaturated hydrocarbons which get oxidised under operating conditions and form gummy products. So antioxidants like amino phenols are used in hydrocarbon oils.

(ii)Boundary lubrication:-

- This type of lubrication occurs when a continuous film of lubricant cannot persist and direct metal to metal is possible.
- In these conditions, the space between the moving or sliding surfaces is lubricated so that a thin layer of lubricant is adsorbed on the metallic surfaces due to physical or chemical forces.
- This adsorbed layer helps to avoid the direct metal to metal contact between the rubbings surfaces.
- This load is carried by the layers of adsorbed lubricant on both thre metal surfaces.
- The coefficient of friction varies from 0.05 to 0.15.

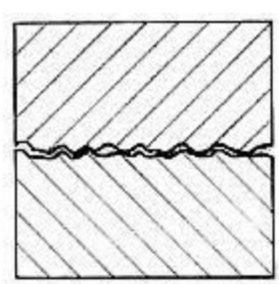


Figure 1: Boundary Lubrication

For boundary lubrication, the lubricant molecules should have

Long hydrocarbon chains,

Polar groups to promote wetting or spreading over the surface,

Lateral attraction between the chains,

Active functional groups which can form chemical bonds with metals or other surface,s

High viscosity index,

Good oiliness,

Resistance to heat and oxidation,

Low pour point.

Solid lubricants, greases and oils with proper additives function as lubricants in this type of lubrication. For example, graphite, molybdenum disulphide, mineral oils with additives of fatty acids or fatty oils, vegetable and animal oils and their soaps. These materials form films on the metal surfaces having internal friction. So they can bear compression and high temperatures.

(iii) Extreme pressure lubrication:-

- When the moving or sliding surfaces are under high pressure and speed, a special type of lubricants is used called high pressure lubricants.
- They withstand high temperatures generated due to friction.
- Under these conditions, liquid lubricants fail to stick and decompose and may vaporise.
- These problems are minimised by adding special additives to mineral oils.
- These additives form durable films on metal surfaces which can withstand high loads and high temperatures.
- Important additives are organic esters as chlorinated esters, sulphur as in sulphurised oils or phosphorous as in tricresyl phosphate.
- These compounds react with metallic surfaces at high temperatures and form metallic chlorides, sulphides or phosphides.
- These metallic compounds possess high melting points and serve as good lubricants at high temperatures and high pressures.

Q6. Write short notes on the following properties of lubricants: (a) Cloud and Pour point (b) Flash and Fire point.

Mechanical properties of lubricants:-

Cloud and pour points:- The lubricating oils obtained from petroleum contains dissolved paraffin wax and asphaltic or resinous impurities which separate out of the oil at low temperatures. Further solidification of lubricant causes jamming of machine.

Cloud point:-When oil is cooled slowly, the temperature at which it becomes cloudy or hazy in appearance is called its cloud point.

Pour point:-When oil is cooled slowly, the temperature at which it ceases to flow or pour is called its pour point.

The cloud and pour points indicate the suitability of lubricants in cold conditions. In machines working at low temperatures, the lubricants that are used should have low pour points. Examples are refrigerator plants and air-craft engines, which are required to start and operate at sub-zero temperatures.

Significance of cloud and pour point:-

(i) Cloud point is useful for estimating the temperature at which filter screens in the fuel intake system of diesel engines become clogged because of separation of wax.

(ii) Pour point values of petroleum and non-petroleum lubricants are necessary under sub-freezing conditions.

Flash and fire points:-

- A good lubricant should have flash point above the temperature at which it is used.
- It should not volatilise under working temperature. If some volatilisation occurs, the vapours should not form inflammable mixture with air.
- This aids in precautionary measures against fire hazards during the use of lubricant.

Flash point:-The lowest temperature at which the oil lubricant gives off vapours that ignites for a moment, when a flame is brought near it.

Fire point:- The lowest temperature at which the vapours of the oil burn continuously for at least five seconds, when a flame is brought near it.

The fire points are mostly 5 to 40^{o}c higher than the flash points. The fire and flash points do not have importance in lubricating properties but are important only when oil is exposed to high temperatures.

Q7. What are viscosity & viscosity index of lubricating oil?

Viscosity:-Viscosity is the property of a fluid by virtue of which it offers resistance to its own flow. It is the indicator of flow ability of a lubricating oil.

Lower the viscosity, greater the flow ability. Viscosity helps in the selection of good lubricating oil. Viscosity helps in the selection of good lubricating oil. Light oils have low densities and easy flow abilities and are used on parts moving a high speed. Heavy oils are used on parts moving at slow speed under heavy loads.

Viscosity index:- The variation of viscosity of a liquid with temperature is called viscosity index.

The viscosity of a good lubricating oil should not change much with change in temperature. But in general, for every 1^{o}C rise in temperature, the viscosity index decreases by 2%.

$$\text{Viscosity Index(VI)} = \frac{L-U}{L-H} \times 100$$

Where, U = viscosity of test oil at 38^{o}c.

L = viscosity of standard oil at 38^{o}c having a VI of zero.

H = viscosity of standard oil at 38^{o}c having a VI of 100.

Q8. Define Refractories and what are the criteria for a good refractory?

Refractories:-

- A substance that is difficult to fuse is called a refractory.
- A refractory is a material which does not melt easily and its fusion temperature is very high. They are inorganic materials which can with stand high temperatures, abrasive and corrosive action with out any deformation in shape.
- The main role of a refractory is to confine heat in it.
- Refractories are widely used for providing high temperature resistant lining for furnaces, kiln, crucibles etc.
- They are used in industries like glass, ceramic, oil-refining, power generation and cement.
- They are also used in the manufacture of rocket nozzles, launch pads and for domestic heating.
- Refractories are available in different shapes and sizes as crucibles, tubes, granules and cements.

Q9. Give the classification of refractories with suitable examples.

Classification:-

Based on fusion temperature, they are of 3 types:

(a) Normal refractories:-They have fusion temperature in the range of 1580-1780^{o}c.

Eg:- fire clay

(b) High refractories:- They have fusion temperature in the range of 1780-2000^{o}c.

Eg;- chromite

(c) Super refractories:- They have fusion temperature in the range of about 2000^{o}c.

Eg:- zircon

Based on chemical composition, they are of 3 types:

(a) Acidic refractories:- They consists of acidic materials like alumina and silica. These refractory materials are resistant to acid slags and are readily attacked by basic slags.

Eg:- Alumina, silica and fire clay refractories.

(b) Basic refractories:- They consist of basic materials like CaO, MgO etc. and are resistant to basic slags. They are widely used in steel making open hearth furnaces.

Eg:- magnesite and dolomite bricks

(c) Neutral refractories:- They are made from weakly basic or acidic materials like carbon, zirconia and chromite. Neutral refractories show resistance to the action of basic and acidic materials. They show good chemical stability.

Eg:-graphite, zirconia and carborundum

Based on oxide content, the refractories are classified in to 3 types.

(a) Single oxide refractories:- Eg:- alumina, magnesia and zirconia

(b) Mixed oxide refractories:- Eg:- zircon, spinel.

(c) Non oxide refractories:- Eg:- Borides, carbides, silicides etc.

Q10. Write short notes on characteristics and properties of refractories.

Characteristics of refractory materials:-

- A good refractory material should have a softening temperature higher than operating temperatures.
- They should be chemically inert.
- The refractoriness should be high for a good refractory.
- The refractories should not crack at operating temperatures.
- They should have low permeability.
- They should have low thermal coefficient of expansion and should expand and contract uniformly with increase and decrease of temperatures.
- They should with stand heavy loads.
- They should possess good physical, chemical and mechanical properties.

Properties of refractories:-

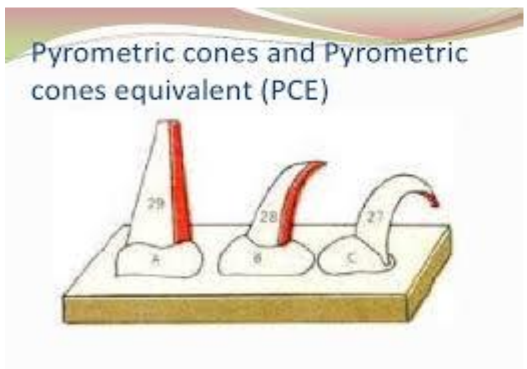
(i)Refractoriness:-

- It is the ability of a material to with stand high temperature without deformation under working conditions.

- It is the softening temperature of the material.
- Higher the softening temperature, more valuable is the refractory.
- The prime function of a refractory is to withstand high temperatures. So its softening temperature should be above the operating temperature.

Measurement of refractoriness:

It is determined by pyrometric cone or segar cone test. The test refractory in the form of a cone(38 mm height &19 mm base) is kept along with similar sized standard cones. They are heated uniformly at 10^0C per minute .Each standard cone is made of a particular refractory with a definite softening temperature. These standard cones are assigned certain numbers with increasing softening temperature. When the test cone softens and loses its shape, one of the standard cones whose softening temperature is close to the test cone will also soften. The serial number of this standard cone will be the Pyrometric cone equivalent (PCE) of the test cone. If the test cone softens earlier than one and latter than next, the PCE value of the test cone is measured as the average of the two.



ii)Refractoriness under load (RUL):-

- Refractoriness determines the strength of a refractory.

  The essential qualities of a refractory are temperature resistance and load bearing capacity.
- The refractory lined furnaces are generally charged with heavy reactants. So they should with stand heavy loads at high temperatures.

Eg:- Fire clay refractories collapse at temperatures below their fusion temperatures when heavy load is applied. Silica refractories with stand loads even at high temperatures.

RUL test is performed to know the safe upper temperature limit up to which the refractory can be used. The RUL test is done in rectangular container by applying a load of 75 kg/cm^2 on to the refractory and heating at a constant rate of 10^oC per minute. During this process, the specimen will soften and its height will decrease under the load. This decrease in height is measured and when there is 10% decrease to that of original height, the temperature is noted. The RUL is then expressed as the temperature at which this 10% deformation occurs.

iii) Thermal conductivity:- In the industrial applications, refractory materials of both high and low thermal conductivity are required depending on the type of furnace. The conductivity of a refractory depends on its chemical composition and porosity. As porosity increases the thermal conductivity decreases because the entrapped air in the pore functions as insulator. Dense refractories have high thermal conductivity.

Most of the furnaces are lined inside with refractory material of low thermal conductivity to reduce heat loss to outside. Eg: fireclay & silica. In muffle furnaces, construction of retorts, the heat should be transmitted. So carbon and silicon carbide refractories which are poor conductors are used.

iv) Thermal spalling:- It is peeling, cracking, fracturing and breaking of refractories due to rapid fluctuations in temperature causing uneven stress and strain in the refractory. A good refractory should have good resistance to thermal spalling.

Spalling can be minimised by:

a) Avoiding sudden fluctuations in temperature.

b) Proper selection of refractory material with high thermal conductivity, uniformity and high porosity. c) by over firing the refractory materials. d) improved furnace design to minimise stress and strain during operation.