



## Module 6: Engineering Materials

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### Module outline:

Introduction

Setting and hardening of cement

Applications of cement

Plaster of paris

Lubricants- Classification

Mechanism and applications of luricants

## 6.1. CEMENT

Cement is the one of the most important building material at the present time. It is used in the construction of buildings, roads, bridges, dams etc. It was discovered, in 1824, by an English Mason, Joseph Aspdin who observed that when strongly heated mixture of limestone and clay was mixed with water and allowed to stand, it hardened to a stone like mass which resembled Portland rock a famous building stone of England. Since then the name Portland cement has been given to a mixture, containing high percentage of lime with silica, iron oxide, alumina, etc.

Cement is a dirty greyish heavy powder containing calcium aluminates and silicates. The silicates and aluminates which form more than 90% of the cement are:

- |    |                             |   |
|----|-----------------------------|---|
| 1. | Tricalcium Silicate         | $3\text{CaO}.\text{SiO}_2$                                |
| 2. | Dicalcium Silicate          | $2\text{CaO}.\text{SiO}_2$                                |
| 3. | Tricalcium Aluminate        | $3\text{CaO}.\text{Al}_2\text{O}_3$                       |
| 4. | Tetracalcium Aluminoferrite | $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ |

Of these, tricalcium silicate is most important.

## 6.2. COMPOSITION OF PORTLAND CEMENT

The approximate composition of Portland cement is:

- |    |                  |                           |          |
|----|------------------|---------------------------|----------|
| 1. | Calcium oxide    | $\text{CaO}$ ,            | 50-60%;  |
| 2. | Silica           | $\text{SiO}_2$ ,          | 20-25%;  |
| 3. | Alumina          | $\text{Al}_2\text{O}_3$ , | 5-10%;   |
| 4. | Magnesium oxide  | $\text{MgO}$ ,            | 2-3%;    |
| 5. | Ferric oxide     | $\text{Fe}_2\text{O}_3$ , | 1-2% and |
| 6. | Sulphur trioxide | $\text{SO}_3$ ,           | 1-2%.    |

For a good quality cement, the ratio of silica ( $\text{SiO}_2$ ) to alumina ( $\text{Al}_2\text{O}_3$ ) should be between 2.5 and 4 and the ratio of lime ( $\text{CaO}$ ) to the total of the oxides of silicon ( $\text{SiO}_2$ ) aluminium ( $\text{Al}_2\text{O}_3$ ) and iron ( $\text{Fe}_2\text{O}_3$ ) should be as close as possible to 2.

## 6.3. RAW MATERIALS

The important raw materials needed for the manufacture of cement are:

1. Limestone – This provides lime.
2. Clay – This provides alumina and silica.
3. Gypsum.

## 6.4. FUNCTIONS OF THE INGREDIENTS OF CEMENT

1. **Lime** is the principal constituent of cement. Its proportions must be properly regulated. However, excess of lime reduces the strength of cement, because it makes the cement to expand and disintegrate. On the other hand, presence of lesser amount of lime than required also reduces the strength of cement and makes it quick setting.
2. **Silica** imparts strength to cement.

3. **Alumina** makes the cement quick setting. Excess of alumina, however, weakens the cement.
4. **Calcium sulphate** (gypsum) helps to retard the setting action of cement. It actually enhances the initial setting time of cement.
5. **Iron oxide** provides: (i) colour, (ii) strength and (iii) hardness to the cement.
6. **Sulphur trioxide**, in small proportion is desirable. When present in small amount, it imparts soundness to cement. However, its excess reduces the soundness of cement.
7. **Alkalis**, if present in excess, cause the cement efflorescent.

## 6.5. MANUFACTURE

These are two processes in use for the manufacture of cement

1. Dry process
2. Wet process

**1. Dry Process:** The process is used when limestone is hard in nature. The lime stone is first broken into small pieces. It is then mixed with clay in proper proportions. The mixture is finally pulverised to such an extent that it passes through 100 mesh sieve. This homogeneous mixture is known as raw meal.

**2. Wet Process:** The process is used when limestone and clay both are soft in nature. The clay is washed with water in wash mill to remove foreign materials like flint. The powdered limestone is mixed with clay paste in the ratio of 75% (limestone) and 25% (clay). The mixture is finally ground and made homogeneous. The homogeneous paste is known as slurry. It contains 40% (approximately) water.

## 6.6. CALCINATION IN ROTARY KILN

It involves *calcination* of the mixture of limestone and clay. *Dry mixture* from the dry process or the *slurry* from the wet process is fed into the rotary kiln (Fig. 6.1) for calcination. Rotary kiln consists of a steel cylinder lined with fire bricks. It is 45-120 m long and has about 3 m internal diameter. The kiln is inclined at an angle of about 15 degrees to the horizontal and it rotates on its axis at the rate of half to one revolution per minute. The charge is introduced at upper end and it travels down as the kiln rotates.

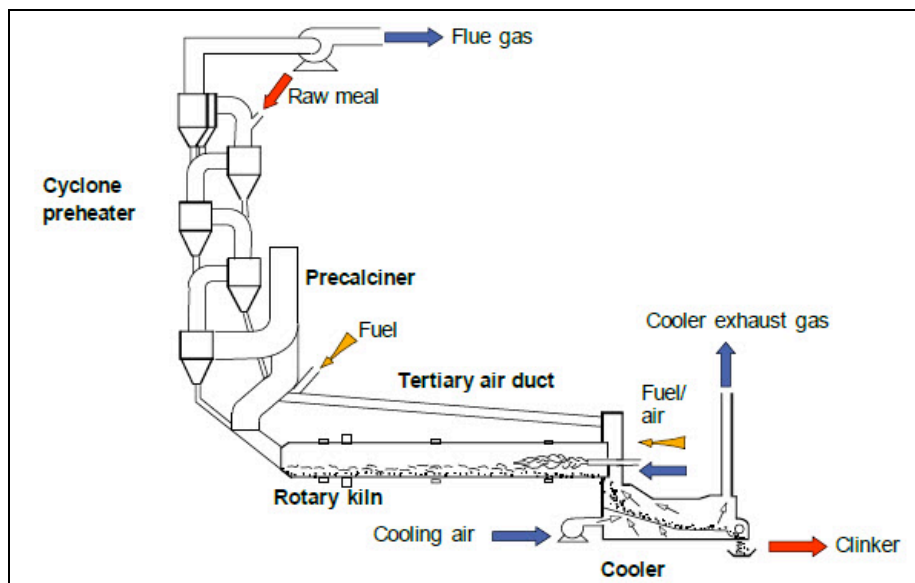
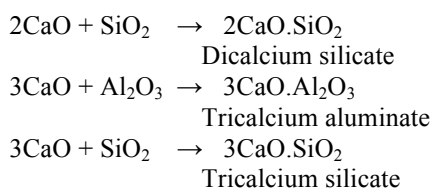


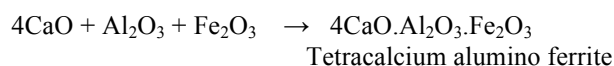
Fig. 6.1: Rotary kiln for manufacture of portland cement.

The charge is heated by burning *fuels* like *pulverized coal* or, *fossil fuel*, or *oil* or *natural gas*. The hot fuel gases are made to enter at the lower end of the kiln with the help of a blower. As the charge moves forward, it meets higher temperatures till it reaches the lower end where the temperature is highest (around 1400°C). The charge takes 2 to 3 hours to cover the journey in the kiln. Reactions taking place in the rotary kiln in three major zones are as follows:

1. **Maximum Temperature Zone (1000°C-1500°C):** The main reactions between lime, alumina and silica takes place near the lower end of kiln resulting in formation of calcium silicates and aluminates as shown below.



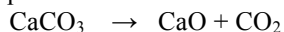
## Advanced Scientific Research



2. **Moderate Temperature Zone (up to 800°C):** At 100°C, the removal of free moisture takes place. At 500°C, kaolin ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) present in clay breaks up into amorphous silica and alumina.

3. **Average Temperature Zone (up to 800°C-1000°C)**

Limestone decomposes to form lime and carbon dioxide.



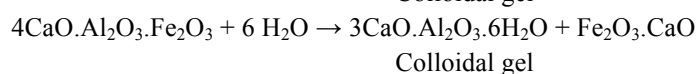
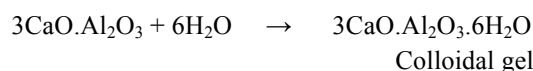
Moreover, due to high temperature in this zone, about 20-30% of mass melts and combines with solids mass to form pebbles (which vary in size) and are called cement clinkers. The burnt gases (containing a good amount of dust) are made to pass through a dust chamber, where most of dust is retained and gases are allowed to escape through chimney. The hot clinkers from the rotary kiln go to coolers which consist of series of tubes parallel to kiln in which air is forced through. As a result of this, the clinkers cool down while the air gets heated. The hot air is then used for the combustion of the fuel as an economy measure.

### 6.7. FORMATION AND PACKING OF CEMENT

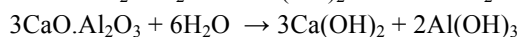
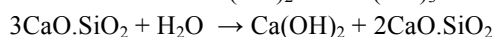
The cooled clinkers are mixed with 3-5% of gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , along with certain dispersing and water proofing agents and then ground to a fine powder. Since pure finely powered, clinkers set very rapidly, therefore, gypsum has to be added to retard the setting of cement. The powdered material is passed through fine sieves and finally it is sent to the automatic packing machines where it is packed in jute or polythene bags.

### 6.8. SETTING OF CEMENT

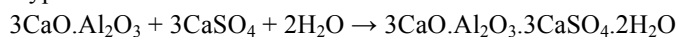
When cement is mixed with water and left as such for some time, it becomes a hard mass. This is known as **setting of cement**. The setting of cement is complicated process, the exact mechanism of this setting process is not known. It is believed that various aluminates and silicates present in the cement form hydrates with water which separate in the form of gel



At the time some  $\text{Ca}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  are formed as precipitates due to hydrolysis.



Gypsum combines with tricalcium aluminate to form calcium sulpho-aluminate,



This reaction slows down the setting. The gels formed start losing water partly by evaporation and partly by forming hydrates with anhydrous constituents. This results in the formation of a hard mass of  $\text{Ca}(\text{OH})_2$  that binds the particles of calcium silicate together, while  $\text{Al}(\text{OH})_3$  fills the interstices resulting in hardening of the mass. Setting of cement is an exothermic process. Hence, cement structures have to be cooled during setting by sprinkling water.

### 6.9. CONCRETE

A mixture of cement, sand, gravel or small pieces of stone and water is known as concrete. It sets to an exceedingly hard structure. It is mainly used for construction of floors. If the cement concrete is filled in an around a wire netting or skeleton of iron rods and allowed to set, the resulting structure is known as reinforced concrete. These structures have great strength and are used for construction of roofs, bridges etc.

### 6.10. REINFORCED CONCRETE CONSTRUCTION (R.C.C.)

The combination of steel and concrete produces structure, called Reinforced concrete construction (R.C.C.), which can bear all types of loads. Reinforced concrete work is mostly used in floor-beams, piers, lintels, girders, arches, slabs, bridges, etc.

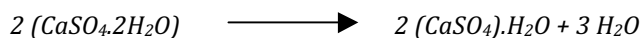
### 6.11. ADVANTAGE OF R.C.C. OVER PLAIN CONCRETE

1. R.C.C. is easier to make and cast into any desired shapes, which can bear all types of loads.
2. It possesses greater rigidity, moisture and fire resistance.
3. Steel reinforcement also tends to distribute the shrinkage cracks, thus preventing the formation of large cracks.
4. Its maintenance cost is practically negligible.

## 6.12. PLASTER OF PARIS, $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ OR $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ (CALCIUM SULPHATE HEMIHYDRATE)

### 6.13. PREPARATION

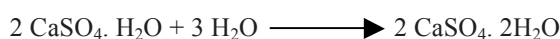
It is hemihydrates of calcium sulphate. It is obtained when gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , is heated to 393 K.



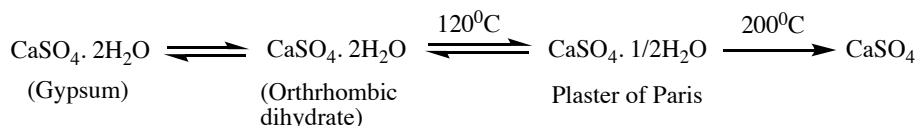
Above 393 K, no water of crystallization is left and anhydrous calcium sulphate,  $\text{CaSO}_4$  is formed. This is known as 'dead burnt plaster'.

### 6.14. PROPERTIES

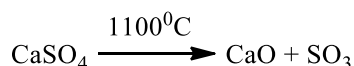
Plaster of Paris is a white powder. It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes. It is due to this reason that it is called plaster. The setting process is exothermic. The addition of common salt accelerates the rate of setting, while a little borex or alum reduces it. The setting of Plaster of Paris is believed to be due to rehydration and its reconversion into gypsum.



The effect of heat on gypsum or the dihydrate presents a review of interesting changes.



At very high temperature ( $1100^\circ\text{C}$ ) anhydrous calcium sulphate decomposes into calcium oxide and sulphur trioxide.



### 6.15. USES

The largest use of Plaster of Paris is in the building industry as well as plasters. It is used for immobilising the affected part of organ where there is a bone fracture or sprain. It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

### 6.16. LUBRICANT

Any substance introduced between two moving or sliding surfaces with a view to reduce the frictional resistance between them is known as a **lubricant**. The process of reducing frictional resistance between moving/ sliding surfaces by the introduction of lubricants in between them is called **lubrication**.

### 6.17. CLASSIFICATION OF LUBRICANTS

Lubricants can be broadly classified, on the basis of physical state, as follows:

1. Liquid lubricants or lubricating oils
2. Semi-solid lubricants or grease
3. Solid lubricants.

#### 6.17.1. Lubricating Oils

Lubricating oils reduce friction and wear between two moving/ sliding metallic surfaces by providing a continuous fluid film in between them. Lubricating oils are further classified as:

- i. Animal and vegetable oils
- ii. Mineral or petroleum oils
- iii. Blended oils (synthetic emulsion)

#### 6.17.2. Greases or Semi- Solid Lubricants

Lubricating greases is a semi-solid, consisting of a soap dispersed throughout liquid lubricating oil. Greases are prepared by saponification of fat with alkali, followed by adding hot lubricating oil while under agitation. Greases have higher shear or frictional resistance than oils and, therefore, can support much heavier loads at lower speeds. They also do not require as much attention unlike the lubricating liquids. But greases have a tendency to separate into oils and soaps.

### 6.17.3. Dry lubricants or solid lubricants

The materials which despite being in the solid phase are able to reduce friction between two surfaces sliding against each other without the need for a liquid medium. They offer lubrication at temperatures higher than liquid and oil-based lubricants operate. The four most commonly used solid lubricants are Graphite, Molybdenum disulfide, Hexagonal boron nitride (white graphite), Tungsten disulfide.

## 6.18. MECHANISMS OF LUBRICATION

There are mainly three types of mechanism by which

### 6.18.1. Fluid-film or Thick-film or Hydrodynamic lubrication

In this, the moving/ sliding surfaces are separated from each other by a thick-film of fluid (at least 1000 Å thick), so that direct surface to surface contact and welding of junctions rarely occurs. The lubricant film covers/ fills the irregularities of the sliding/ moving surfaces and forms a thick layer in between them, so that there no direct contact between the materials surfaces (Fig. 6.2). This consequently reduces wear. The resistance to movement of sliding/ moving parts is only due to internal resistance between the particles of the lubricant moving over each other.

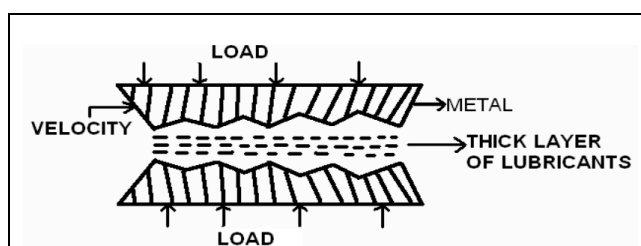


Fig. 6.2: Fluid film lubrication or Hydrodynamic lubrication

Delicate instruments, light machines like watches, clocks, guns, sewing machines, scientific instruments, etc. are provided with the types of lubrication. Hydrocarbon oils are considered to be satisfactory lubricants for fluid-film lubrication.

### 6.18.2. Boundary lubrication or Thin-film lubrication

When a continuous film of lubricant cannot persist and direct metal to metal is possible due to certain reasons. This happens when:

- i. A shaft starts moving from rest.
- ii. The speed is very low.
- iii. The load is very high
- iv. Viscosity of the oils is too low. Under such conditions, the clearance space between the moving/ sliding surfaces is lubricated with an oil lubricant, a thin layer of which is adsorbed, (i.e., surface attached) by physical or chemical forces or both are both the metallic surfaces. These adsorbed layers avoid direct metal to metal contact. The load is carried by the layers of the adsorbed lubricant on the both metal surfaces (Fig. 6.3).

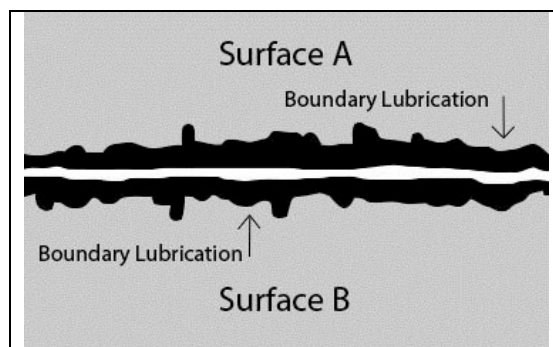


Fig. 6.3: Boundary lubrication

Vegetable and animal oils (glycerides of higher fatty acids), graphite or molybdenum disulphide either alone or as stable suspension in oil is also used for boundary lubrication. These minerals form films on the metal surfaces, which possess low internal friction and can bear compression as well as high temperatures.

### 1.18.3. Extreme pressure lubrications

When the moving / sliding surfaces are under very high pressure and speed, a high local temperature is attained and under such conditions, liquid lubricants fail to stick and many decompose and even vaporize. To meet these extreme pressure conditions,

special additives are added to mineral oils. These are called “**extreme pressure additives**”. These additives form one metal surfaces more durable films, capable of withstanding very high loads and high temperatures. Important additives are organic compounds having active radical or groups such as chlorine (as in chlorinated esters), sulphur (as in sulphurized oils) or phosphorus (as in tricresyl phosphate).

## 6.19. PROPERTIES OF LUBRICANTS

1. **Viscosity** is the property of a liquid or fluid by virtue of which it offers resistance to its own flow. Viscosity should not be too low or too high. (Viscosity is inversely proportional to temperature).
2. **Flash - Points and Fire - Points:** Flash Point is the lowest temperature at which the oil lubricant gives off enough vapour that ignites for a moment, when a tiny flame is brought near it, while fire point is the lowest temperature at which the vapour of the oil burn continuously for at least five seconds, when a tiny flame is brought near it.
3. **Oiliness** of a lubricant is a measure of its capacity to stick on to the surfaces of machine parts, under conditions of heavy pressure or load. For high pressure, high oiliness oil should be used. It is important for extreme pressure lubrication.
4. **Cloud and Pour points:** When oil is cooled slowly, the temperature at which it becomes cloudy or hazy in appearance, is called its cloud point; while the temperature at which the oil ceases to flow or pour, is called its pour point.
5. **Volatility:** Good lubricant should have low volatility. It is measured by vaporimeter.
6. **Emulsification** is the property of oils to get intimately mixed with water, forming a mixture, called emulsion.
7. **Carbon residue:** Normally lubricants consist of high percentage of carbon containing compounds. Lubricants decompose due to raise in temperature and deposit carbon creating problems to internal combustion engines and Air compressors. A good lubricant should deposit least amount of the carbon.
8. **Decomposition stability:** Lubricating oils must be stable to decomposition at the operating temperatures by oxidation, hydrolysis and pyrolysis.
9. **Aniline point:** The minimum equilibrium solution temperature for equal volumes of aniline and oil sample. Good lubricating oil should have higher aniline points. Higher A.P means higher percentage of paraffinic hydrocarbons and hence lower percentage of aromatic hydrocarbons.
10. **Precipitation Number:** The percentage of asphalt present in oil. Precipitation Number is used to differentiate the different classes of lubricants.
11. **Saponification number:** Number of milligrams of KOH required to saponify 1g of oil.
12. **Mechanical stability:** At very high pressures of operation, the stability of a lubricant is judged by four balls extreme pressure lubricant test.
13. **Neutralization Number:** Is a scale to determine the amount of acidic or basic constituents of oil. Acid Number is the amount of KOH required in milligrams to neutralize the fatty acids in 1g of oil. Good lubricating oil should possess acid value less than 0.1.

## 6.20. FUNCTIONS OF LUBRICANT

1. It reduces surface deformation, wear and tear, because the direct contact between the rubbing surfaces is avoided.
2. It reduces loss of energy in the form of heat. In other words it acts as coolant.
3. It reduce waste of energy i.e., to increase efficiency of machines.
4. It reduces expansion of metal by local fractional heat.
5. It avoids seizure of moving surfaces, since the use of lubricant minimizes the liberation of frictional heat.
6. It avoids are reduces unsmooth relative motion of the moving/ sliding parts.
7. It reduces the maintenance and running cast of the machine.
8. It also, sometimes, acts as a seal. For example, lubricant used between piston and the cylinder wall of internal combustion engine acts as a seal, thereby preventing also the leakage of gases under high pressure from the cylinder.

## ABOUT THE AUTHORS



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## REFERENCES

1. B. H. Mahan; R. J. Meyers (1998) "University Chemistry" Pearson Education, India.
2. P. C. Jain (2015) "Engineering Chemistry" Dhanpat Rai Publishing Company.

## EXERCISE

### Long Answer Type Questions

1. Write the chemistry of setting and hardening of cement.
2. Name the raw materials necessary for the preparation of Portland cement.
3. Discuss the chemical changes that occur during the setting of cement.
4. Explain the manufacture of cement in detail.
5. How will you manufacture Portland cement by wet process?
6. Write note on concrete and RCC.
7. Define the term lubricants. Mention their important functions. Explain and discuss the significance of any two properties of lubricants.

### Short Answer Type Questions

1. Explain the heat of hydration of cement.
2. What is Plaster of Paris? Write its use.
3. Discuss the classification of lubricants with suitable examples.
4. What are chief functions of lubricants?

### Very Short Answer Type Questions

1. Write a note on lubricants.
2. Write a short account on solid lubricants.
3. What are the functions of lubricants?
4. Discuss in brief lubrication.