CEMENT

Cement is an inorganic binding material which possesses **adhesive and cohesive** properties to bind rigid masses like stones, bricks, building blocks. Cements are **hydraulic in nature** it possesses the property of **setting and hardening** in the presence of water.

Portland cement: Cement is named as portland cement because during setting and hardening of a paste of cement, the colour and hardness resembles to Portland stone. William Aspidin (1824) is recognized as the father of the modern Portland cement industry. Portland cement is a mixture of calcium silicates and calcium aluminates with small amount of gypsum. Portland cement is hydraulic nature and possesses the property of setting and hardening in the presence of water.

TYPES OF CEMENT

1. White cement or white Portland cement: As the name suggests, white cement is white in colour due to the absence of iron oxide. It is obtained by calcining the raw material of Portland cement which is free from iron oxide.

Properties:

i. It is more expensive than ordinary Portland cement.

ii. It act as pore-blocking and water- repelling agents.

Uses: It is used to make concrete which is impervious to water under pressure. It is used in the construction, where absorption of water needs to be avoided. It is used in the construction of bridges and structures under water.

2. Water–proof cement or hydrophobic cement: Water-proof cement is cement obtained by adding water proof substances like calcium stearate, Aluminium stearate and gypsum with tannic acid to ordinary Portland cement during grinding.

Properties:

i. It is more expensive than ordinary Portland cement.

ii. It acts as pore-blocking and water-repelling agent.

Uses: It is used to make concrete impervious to water under pressure. It is used in the construction, where absorption of water needs to be avoided. It is used in the construction of bridges and structures under water.

3. High-alumina cement: High alumina cement is composed of calcium aluminate, hence it is also calcium aluminate cement. It is manufactured by heating a mixture of bauxite, limestone and grinding resulting clinkers.

Properties:

i. It develops high strength within a day. It has more chemical resistance than ordinary cement.

ii. Faster rate of hardening as compared to Portland cement.

Uses: It is used in construction of concrete, where Rapid strength development is required even at low temperatures. It is used as a protective liner against microbial corrosion. Such as in sewer infrastructures.

4. Acid resistant cement: Portland cement as low resistivity to acids, cement can be made acid resistant by mixing with inert acid resisting siliceous materials along with sodium, potassium or silicon esters in appropriate amounts.

Properties:

i. The siliceous materials forms strong bonds with cement and the resulting cement is resistant to acids. It is hard but brittle and becomes porous on drying.

ii. It is not water resistant and fails when attacked by water or weak acids.

Uses: It is used for acid resistance and heat resistance coatings of insulations of chemical industry.

FUNCTIONS OF THE INGREDIENTS IN CEMENT

A good sample of Portland cement has the following ingredients:

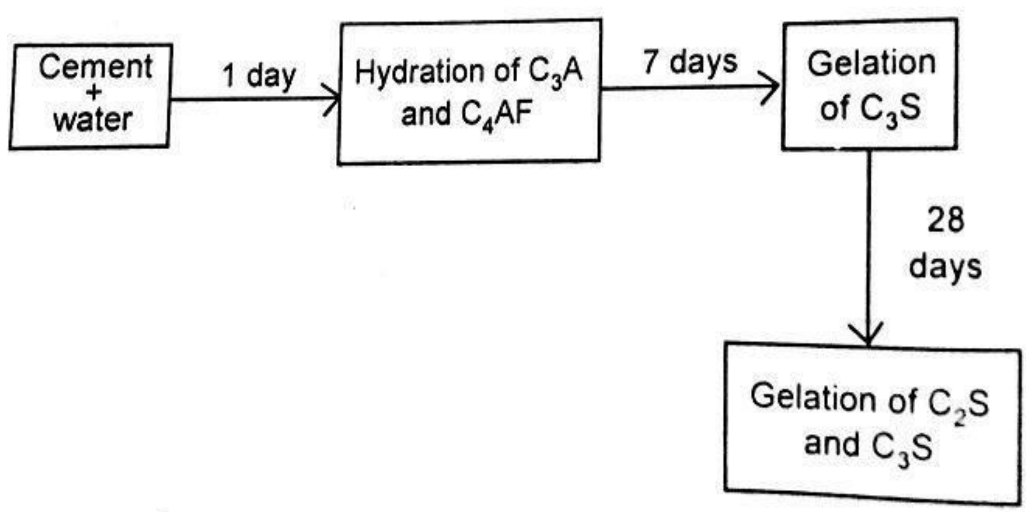
Type of ingredient	Function of ingredient
lime (CaO)	Principle constituent of cement, proportion should be regulated. Excess or lesser amount of lime reduces the strength.
Silica (SiO_2)	It imparts strength to cement.
Alumina (Al_2O_3)	It is responsible for setting action of cement.
Ferric oxide (Fe_2O_3)	It provides colour, strength and hardness to the cement.
Sulphur trioxide (SO_3)	Presence of small amount of SO_3 imparts soundness to cement.
Gypsum ($CaSO_4 . 2H_2O$)	It acts as retarding agent for quick setting of cement.

CHEMICAL COMPOSITION OF PORTLAND CEMENT

Type of the composition	Formula	Symbol	Percentage (%)
Tri calcium silicate	$3CaO. SiO_2$	C_3S	45
Di calcium silicate	$2CaO. SiO_2$	C_2S	25
Tri calcium aluminate	$3CaO. Al_2O_3$	C_3A	10
Tetra calcium alumino ferrite	$4CaO. Al_2O_3. Fe_2O_3$	C_4AF	9
Calcium Sulphate	$CaSO_4$	-	5
Magnesium oxide	MgO	-	4
Calcium oxide	CaO	-	2

SETTING AND HARDENING OF CEMENT

Cement has the property of setting to hard mass after being mixed with water which is called cement paste. After mixing with water, hydration reaction starts and the mass becomes hard and very resistant to pressure and followed by gelation is called as the setting of cement. The first setting takes place within 24 hours. The subsequent hardening requires about a fortnight. Setting is defined as stiffening of the original plastic mass and hardening is development of strength due to crystallization. Both these processes are due to hydration and hydrolysis reactions.



Initial setting: Initial setting of cement involves hydration of Tri calcium aluminate (C_3A) and gel formation of Tera calcium alumino ferrite (C_4AF).

$$3CaO.Al_2O_3 + 6H_2O \longrightarrow \underset{\textbf{Crystalline}}{3CaO.Al_2O_3.6H_2O} + 880Kj/kg$$

$$4CaO.Al_2O_3.Fe_2O_3 + 7H_2O \longrightarrow \underset{\textbf{Crystalline}}{3CaO.Al_2O_3.6H_2O} + \underset{\textbf{Gel}}{CaO.Fe_2O_3H_2O} + 420\ Kj/kg$$

Final setting (between 7 to 28 days):

These gels shrink with passage of time and leave some capillaries for the water to come contact with C_3S and C_2S to undergo further hydration and hydrolysis reactions enabling the development of greater strength over a length of time. Final setting and hardening of cement paste is due to the formation of **Tobermanite gel** plus crystallization of calcium hydroxide and hydrated tri calcium aluminate.

$$2CaO.SiO_2 + H_2O \longrightarrow \underset{\textbf{Tobermanite gel (Metastable)}}{2CaO.SiO_2.H_2O} + 500Kj/kg$$

$$2(3CaO).SiO_2 + 6H_2O \longrightarrow \underset{\textbf{Tobermanite gel (Stable)}}{3CaO.SiO_2.3H_2O} + \underset{\textbf{Crystalline}}{3Ca\ (OH)_2}$$

LUBRICANTS

Lubricants are the substances which reduces the friction when, introduced between two surfaces, and the phenomenon known as lubrication.

Classification of Lubricants: Lubricants are classified on the basis of their physical state:

1. Liquid Lubricants:

Examples: Animal oils, Vegetable oils and Mineral oils.

2. Semi-Solid Lubricants or greases: Grease is a semi solid lubricant obtained by thickening liquid lubricating oil through the addition of a metallic soap. The thickness is usually sodium or calcium or lithium soap.

Examples: Greases and waxes.

3. Solid Lubricants: They are obtained by fractional distillation of crude petroleum oils. **Molybdenum disulphide and graphite** are sand-witch like structure in which a layer of molybdenum atoms lies between two layers of sulphur atoms. The weak Vander Waals forces, acting in between the layers, can be destroyed easily**.** MoS_2 can also be used as power or dispersions. It is effective up to 800 ^{0}C. It is used in wire-drawing dues.

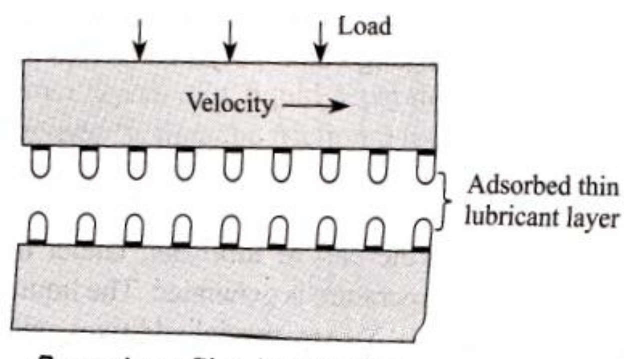
CHARACTERISTICS OF GOOD LUBRICANT

1. The lubricant should keep moving parts apart.
2. It should be reducing friction.
3. It should transfer heat and act as a coolant.
4. It prevents rust and corrosion and thereby reduces the maintenance and running cost of the machines.
5. It acts as a seal.
6. It should also reduce the loss of energy in the form of heat.
7. It should minimize the liberation of frictional heat; the expansion of the metals can be reduced.
8. It reduces unsmooth relative motion of the moving surfaces.

MECHANISM OF LUBRICANTS

a) Boundary lubricants (or) Thin-Film lubrication.
b) Hydrodynamic (or) fluid film (or) Thick-film lubrication.
c) Extreme pressure lubricants.

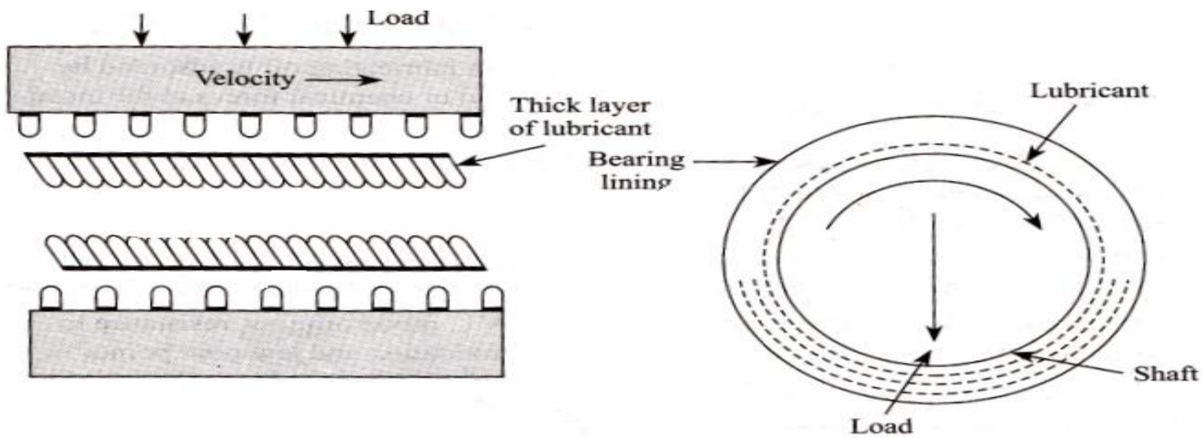
a. Thin-Film (or) Boundary lubrication: Conditions for the thin film lubrication are **High load and slow speed**. When the lubricant is not viscous enough to generate a film of sufficient thickness(less than 1000 A^o) to separate the Surfaces under heavy loads, friction may yet be reduced with the proper lubricant, the co-efficient of friction is 0.05-0.15 such an application is known as boundary lubrication.



Boundary film lubrication

Examples: Graphite and MoS_2, Vegetable and animal oils and their soaps are used for boundary lubrication.

b. Thick-film (or) Hydrodynamic (or) fluid film lubrication: Conditions for the thick film lubrication is **low load and High speed**. In this, the moving/sliding surfaces are separated from each other by a bulk lubricant film (at least 1000 A^o thick). This bulk lubricant film prevents direct surface to surface contact so that the small peaks and valleys do not interlock. The co-efficient of friction is 0.001-0.03. This consequently reduces friction and prevents wear.



Fluid film lubrication

c. Extreme pressure lubrication: Conditions for the extreme pressure lubrication is **high load and High speed**. The friction can be ovoid by incorporating extreme pressure additives. In mineral oils for applications in which high temperature is generated due to high speed of moving/sliding surfaces under high pressure.

Examples: Chlorinated esters, sulphurised oils and tricrysyl phosphate.

PROPERTIES OF LUBRICANTS

1. Viscosity: It is a measure, It is an internal resistance of fluid during its flow, it is expressed in cetipoise.

Determination: The viscosity of oil is determined by Red wood viscometer and Ostwald's viscometer

Significance:

i. The lower the viscosity, greater the flow ability.

ii. If temperature increases viscosity of the lubricating oil decreases.

iii. If pressure increases, viscosity of the lubricating oil increases.

iv. If the viscosity of the lubricating oil is too high the movement of the machine is restricted due to excessive friction.

v. If the viscosity of the lubricating oil is too low, the liquid oil film cannot be maintained and excessive wear will take place.

A good lubricant should have moderate viscosity.

2. Flash and Fire point: The flash point of oil is the lowest temperature at which it gives off vapors that will ignite for a moment when a small flame is brought near it.

The fire point of oil is the lowest temperature at which the vapor of the oil burns continuously for at least 5 seconds, when a small flame is brought near it.

Determination: Flash and fire points can be determined by Open cup (**Cleve Land's**) apparatus or Closed cup (**Pensky Martins**) apparatus.

Significance: The flash and fire points are used to indicate the fire hazards of petroleum products, evaporation losses and the type of lubricant.

A good lubricant should have higher flash and fire point than the operating temperatures.

3. Cloud and pour point: The cloud point of petroleum oil is cooled slowly the temperature at which the oil becomes cloudy in appearance is called **cloud point**.

The temperature at which the oil ceases to flow or pour is called **pour point**.

Determination: Oil is taken in a flat bottomed tube enclosed in an air jacket and it is cooled in a freezing mixture (Ice + $CaCl_2$), then thermometers are introduced into the freezing mixture. As the cooling takes place via the air jacket, temperature of the oil falls.

- The temperature at which the cloudiness appears is noted as the **cloud point**.
- The temperature at which the oil does not flow in the test tube for 5 seconds on tilting it to the horizontal position is noted as the **pour point**.

Significance: Most of the petroleum based lubricating oils contain dissolved paraffins wax and asphaltic impurities. When the oil is cooled these impurities undergo solidification which cause jamming of the machine, so the Cloud and pour points indicate the suitability of the lubricants in cold condition.

A good lubricant should have low cloud and pour point than the operating temperatures.

4. Viscosity Index: Viscosity Index is a measure of how much a fluid's viscosity changes as the temperature of the fluid changes.(The rate change of viscosity with temperature).

Determination: The viscosity index of the test oil is given by the following formula:

Viscosity index = L - U/ L - H × 100 (where **L** is the viscosity of the low V.I oil at 38°C. **U** is the viscosity of the test oil at 38°C. **H** is the viscosity of the high V.I oil at 38°C)

Significance: A good lubricant should have minimum change in viscosity for a wide range of temperature.

A good lubricant should have high viscosity index.

REFRACTORIES

Refractories are ceramic materials that can withstand high temperatures as well as abrasive and corrosive action of molten metal slag's and gases, without suffering a deformation in shape.

Classification of Refractories:

1. Classification based on Temperature: On the basis of fusion temperature these are 3 types:

a. Normal Refractories: Fusion temperature: 1580-1780°C. **Eg:** Fire clay

b. High Refractories: Fusion temperature: 1780-2000°C. **Eg:** Chromite

c. Super Refractories: Fusion temperature: >2000°C. **Eg:** Zerconia

2. Classification based on chemical composition: These are classified into 3 types:

i. Neutral refractories like graphite, zirconia and SiC refractories. These refractories are made from weakly basic/acidic materials like carbon, zirconia (ZiO_2) and chromite ($FeO.CrO_2$).

ii. Acid refractories like alumina, silica and fire clay refractories. These refractories consist of acidic materials like alumina (Al_2O_3) and silica (SiO_2).

iii. Basic refractories like Magnetite and Dolomite refractories. These refractories consist of basic materials like CaO, MgO.

CHARACTERISTICS OF GOOD REFRACTORIES

1. Chemical Inertness: The refractory materials used as lining for furnace should be chemically inert. It should not react with slags, reagents, furnace gases, fuel ashes & products produce inside the furnace. Example: Silica bricks being acidic cannot be used in basic.

2. Refractoriness is the ability of a refractory material to withstand the heat without appreciable softening or deformation under given service conditions.

3. Porosity: Porosity of a refractory material is the ratio of its pore's volume to the bulk volume. Porosity can also increase the thermal shock resistance. The least porous bricks have the highest thermal conductivity, strength, resistance to abrasion and corrosion.

4. Thermal spalling: Rapid changes in temperature, cause uneven expansion and contraction of refractory material, thereby leading to development of internal stresses and strains. This is in turn are responsible for cracking, breaking or fracturing of a refractory brick or block under high temperature, collectively known as thermal spalling.

APPLICATIONS OF REFRACTORIES

1. Refractory is used for the construction of kilns, ovens, crucibles and furnaces.

2. Magnatite refractory used in the construction of electric furnaces, soaking pits, cement kilns.

3. Graphite refractory used in the lining of blast furnace, electrodes, smelting crucibles.

4. Carborundum refractory used in the lining for gas generator.