<u>Cement</u>

- Concrete is a non-metallic composite material of construction used for constructing buildings, bridges, high ways, dams etc.
- The essential bonding material which binds sand and rock when mixed with water in concrete is Cement. Cement possesses adhesive and cohesive properties and is used for binding the building blocks, bricks, stones etc.

Classification of Cement: Four types-

- **Natural Cement:** Made by calcining a naturally occurring argillaceous limestone (limestone consisting predominantly of calcium carbonate, but including 10-40% of clay minerals) and then pulverizing the calcined mass. Calcium silicates and aluminates are formed by the combination of silica and alumina with calcium oxide during calcination. It possesses hydaullic properties and have relatively low strength.
- **Puzzolana Cement:** It is oldest cement invented by Romans. This is made by mixing and grinding of natural puzzulona and slaked lime $Ca(OH)_2$. Natural puzzulona is deposit of volcanic ash which is produced by rapid cooling of lava and lava in turn is a molten mixture of silicates of Ca, Fe and Al. It possesses hydaullic properties.
- **Slag Cement:** It is made by hydrated lime $Ca(OH)_2$ and blast furnace slag. A mixture of Ca and Al silicates is granulated by pouring it into a stream of cold water. Then it is dried and mixed with hydrated lime.
- **Portland Cement:** Also known as 'magic powder' William Aspadin was father of modern Portland cement industry. The name Portland cement was used because on mixing with water, it sets to give a hard, stone-like mass which resembled quarried on the Isle of Portland, England. It is a type of cement, not a brand name. It is a hydraulic cement because they set and harden under water.

PORTLAND CEMENT

Composition: The name of this cement is because of its similar composition with that of Portland rocks of England. The main constituents of Portland cement are:

Lime (CaO) - 50-60%, Silica (SiO_2) - 20-25%, Alumina (Al_2O_3) - 5-10%, Magnesia (MgO) - 2-3%, Iron oxide (Fe_2O_3) - 1-2% and SO_3 - 1-2%

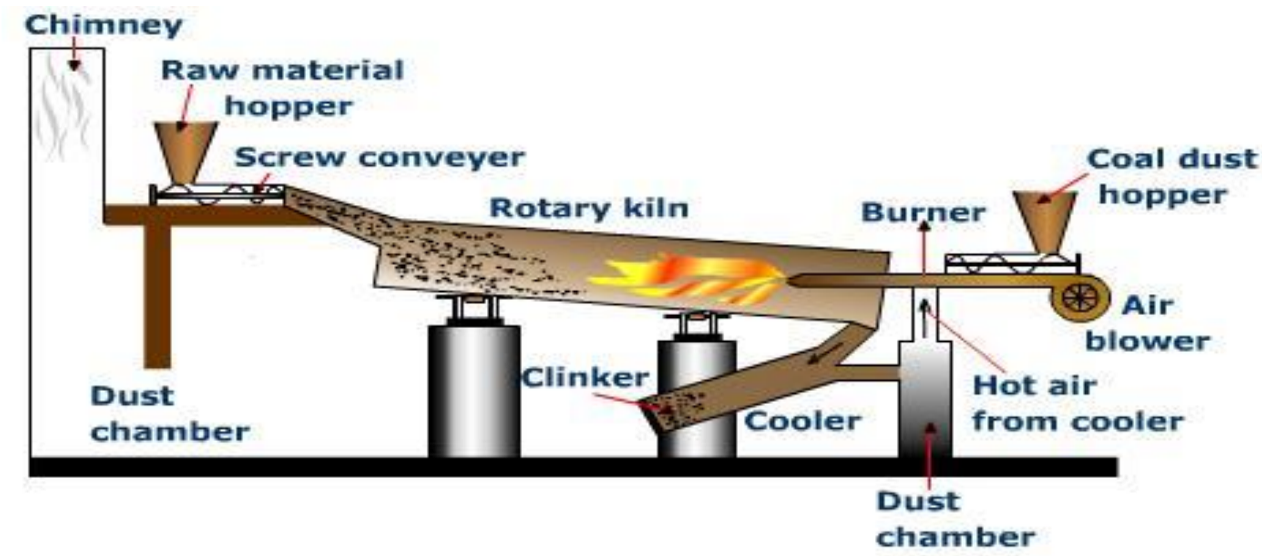
Manufacturing of Portland Cement:

- The main raw materials are lime stone (marble) and clay.
- Lime stone ($CaCO_3$) is the source of lime (CaO) while clay provides SiO_2, Fe_2O_3 and Al_2O_3.
- The manufacturing involves the following steps:

1. **Crushing**: It is the first step in the manufacture of Portland cement. Powdered limestone and clay (3:1) are mixed. Raw materials are crushed by the crushers till the size of raw material reduces ¾ of an inch.
2. **Mixing**: Mixing of the powdered limestone and clay. These are mixed either by dry or wet process. The dry process produces a fine ground powder. It is stored in bins. The wet process (in presence of water) results in a slurry which is mixed and pumped to storage basins.
3. **Grinding**: Grinding the raw material along with 30-40% water to form slurry.

4. **Burning:** Mixture is heated at about 1770-1870 ^{o}C in a **rotary kiln** where actual chemical changes take place. (Rotary kiln is a long steel cylinder, length 30-160 m, diameter 2-4 m, inner lining with firebrick refractory, can be rotated). In the kiln temperature varies between 1100 -1800 ^{o}C.

S. No.	**Dry Process**	**Wet Process**
1	Slow & costly process	Comparatively faster & cheaper process
2	Less fuel consumption, shorter kiln sufficient	Higher fuel consumption, longer kiln required to drive off the water
3	Quality of cement produced is inferior	Superior, as more accurate control of composition can be attained.
4	This process is adopted when the raw materials are quite hard	adopted when the raw materials are soft
5	Not suitable when the principal raw material has 15% or more inherent moisture, then this process becomes uneconomical.	In that case, this process is suitable.



<u>Chemical reactions taking place at various zones of rotary kiln are:</u>

(i) **Drying zone:** In this zone temperature raises to maximum 750 ^{o}C so that entire moisture in the slurry gets evaporated and the clay is broken into Al_2O_3, SiO_2 and Fe_2O_3.

$$Al_2O_3.2SiO_2.Fe_2O_3.2H_2O \longrightarrow Al_2O_3 + 2SiO_2 + Fe_2O_3 + 2H_2O$$

(ii) **Calcination zone**: In this zone, the temperature rises to 1000 ^{o}C and the limestone is completely decomposed into CaO.

$$CaCO_3 \longrightarrow CaO + CO_2 \text{ (Decomposition of limestone)}$$

(iii) **Reaction zone (Clinkering zone):**

The temperature in this zone is about 1600 °C, the mixture is partly fused and chemical combinations between lime, alumina, ferric oxide and silica occur, resulting in the formation of calcium aluminates and silicates.

(a) $2CaO + SiO_2 \longrightarrow 2CaO.SiO_2$ **(Dicalcium silicate) (C_2S)**

(b) $3CaO + SiO_2 \longrightarrow 3CaO.SiO_2$ **(Tricalcium silicate) (C_3S)**

(c) $3CaO + Al_2O_3 \longrightarrow 3CaO.Al_2O_3$ **(Tricalcium Aluminate) (C_3A)**

(d) $4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow 4CaO.Al_2O_3.Fe_2O_3$ **(Tetracalcium Aluminoferrite) (C_4AF)**

5. **Grinding:** The cooled clinkers are ground to fine powder. During grinding 2-4% of gypsum is added. Gypsum and POP act as a retarder to prevent quick setting.
6. **Packaging:** The Portland cement powder is packed in 50 kg bags with the help of machines.

Setting and Hardening of Portland Cement:

When Portland Cement is used, it is mixed with water. It is an exothermic reaction in which cement reacts with water to form gelatinous mass which slowly sets into a hard mass. During dehydration, calcium aluminates and calcium silicates change into their colloidal gels. At the same time some $Ca(OH)_2$ and $Al(OH)_3$ are formed as precipitates due to hydrolysis. $Ca(OH)_2$ binds the particles of calcium silicates together while $Al(OH)_3$ fills the pores making the mass impervious.

Reactions involved during Setting and Hardening of Portland Cement are:

(I) Initial Setting: (Reaction in 1 day)

$$4\,CaO.\ Al_2O_3.Fe_2O_3 + 7H_2O \rightarrow \underset{\text{(Hydrated Tricalcium aluminate)}}{3CaO\ Al_2O_3.6H_2O} + CaO.\ Fe_2O_3.\ H_2O + 420\ kJ/Kg$$

$$3CaO.\ Al_2O_3 + \underset{\text{(Gypsum)}}{x(CaSO_4.2H_2O)} \rightarrow \underset{\text{(Tricalcium sulphoaluminate) (x=32)}}{3CaO.\ Al_2O_3.\ xCaSO_4.2H_2O}$$

(II) Reaction taking place between 1 to 7 days:

$$3CaO.SiO_2 + xH_2O \rightarrow Ca(OH)_2 + \underset{\text{(Hydral gel)}}{2CaO.\ SiO_2.(x\text{-}1)H_2O} + Heat$$

(III) Final setting between 7 to 28 days:

$$2CaO.SiO_2 + x\ H_2O \rightarrow \underset{\text{(Tobermonite gel)}}{2CaO.SiO_2.x\ H_2O} + 500\ KJ/kg$$

Role of Gypsum:

- The presence of gypsum in the cement helps to retard the speed of the initial set.
- Gypsum combines with tricalcium aluminate to form calcium sulphoaluminate.
- The removal of fast setting tricalcium aluminate results in slowing down the setting process.

$$3CaO.Al_2O_3 + \underset{\text{Gypsum}}{3CaSO_4.2H_2O} \longrightarrow \underset{\text{Tricalcium sulphoaluminate}}{3CaO.Al_2O_3.3CaSO_4.2H_2O}$$

Physical properties of Portland Cement:

(i) **Fineness:** It affects the hydration of cement. Finer the grains of cement, higher is the surface area, faster is the hydration. But too fine particles increase the pre-hydration due accidental contact with moisture during manufacturing and storage. In general, finer a cement, higher the heat of hydration resulting in accelerated strength gain.

(ii) **Soundness:** Ability of a cement to maintain a stable volume after setting. A sound cement resists cracking, disruption and disintegration of the material mass. (An unsound cement has excessive amounts of free lime which is enclosed in cement particles. After the cement has set, if moisture reaches the lime, lime expands with considerable force, disrupting the set cement).

Deterioration/Decay of Cement:

The cement constituents are susceptible to attack by salty water and other acidic solutions. When the surface is impermeable, the rate of attack will be slow.
Acidic water can attack the cement structures. With decrease of pH (on increase of acidity), the rate of attack increases. Dissolved CO_2 or presence of other organic and inorganic acids are responsible for acidity of water.

Decay of cement is due to:

(i) The leaching out of free lime from it. This leaching is due to the chemical action of CO_2 present in acidic water.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$
$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$
$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$$

(ii) Hydrolysis of silicate and aluminates.

Prevention: Decay of cement can be minimized by coating the surface by paints and dry oils.

PLASTER OF PARIS: $(CaSO_4).1/2H_2O$

- The hemi hydrate form of calcium sulphate is known as Plaster of Paris.
- The molecular formula of Plaster of Paris is $2CaSO_4.H_2O$ or $CaSO_4.\ 1/2\ H_2O$.

Preparation: It can be prepared by heating gypsum at 393 K.

$$\underset{\text{Gypsum}}{2(CaSO_4.2H_2O)} \xrightarrow{393\ K} \underset{\text{Plaster of Paris}}{(CaSO_4)_2.H_2O + 3H_2O}$$

The temperature should not be raised because at 473 K the whole of water is lost and anhydrous salt left is called Dead Burnt Plaster. It has no setting property.

Setting and Hardening of POP: On mixing with water, it forms a plastic mass which sets into a hard solid in 5-15 minutes. This is called setting of POP.

$$(CaSO_4)_2.H_2O + 3H_2O \longrightarrow \underset{\text{Gypsum}}{2(CaSO_4.2H_2O)}$$

POP forms a plastic mass when it is mixed with water. This plastic mass quickly sets or hardens as ($CaSO_4.2H_2O$). During setting, it slightly expands and regains the closely-packed crystalline structure of gypsum.

Applications of POP:

(i) Used for making moulds for pottery, ceramics etc.
(ii) For making statues, models and other decoratives.
(iii) Used in surgical bandages known as plaster for setting the broken and fractured bones in the body.