CEMENT

Cement is a substance which sets to a hard mass in presence of water. It holds concrete together, which means that it is extremely, widely used in our society. It has been manufactured in New Zealand for more than 100 years and during this century production has increased one hundred-fold. These natural cements are nothing but a mixture of burnt silicates and lime. The artificially made cement of quick setting and of much greater strength is called Portland cement. It was first made by Joseph Aspdin in 1824. The name was derived from the Portland stone found in Portland Island near England.

Types of Cements: There are over ten different types of cements that are used in construction purposes and they differ by their composition and are manufactured for different uses. These are **rapid-hardening cement** (RHC), **quick-setting cement** (QSC), **low-heat cement** (LHC), **sulphate-resisting cement** (SRC), **blast furnace slag cement** (BFSC), **high-alumina cement** (HAC), **white cement** (WC), **coloured cement** (CC), **pozzolanic cement** (PzC), **air-entraining cement** (AEC), and **hydrophobic cement** (HpC). RHC has increased the lime content compared to the Portland cement (PC). Purpose of having high lime content is to attain high strength in early days. It is used in concrete when formwork is to be removed early.

Raw Materials for Portland Cement Manufacture: The raw materials and their percentages are shown below.

Calcium oxide, CaO	61–67%
Silicon dioxide, SiO_2	19-23%
Aluminium oxide, Al_2O_3	2.5-6%
Ferric oxide, Fe_2O_3	0-6%
Sulfur (VI) oxide, SO_3	1.5-4.5%

Composition of Portland Cement:

Tricalcium silicate $(CaO)_3.\ SiO_2$	C_3S	45-75%
Dicalcium silicate $(CaO)_2.\ SiO_2$	C_2S	7–32%
Tricalcium aluminate $(CaO)_3.\ Al_2O_3$	C_3A	0–13%
Tetracalcium aluminoferrite $(CaO)_4\ .Al_2O_3.\ Fe_2O_3$	C_4AF	0–18%
Gypsum $CaSO_4.\ 2H_2O$	CSH_2	2–10%

Setting and hardening of cement:

When cement is mixed with water it 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 crystallization.

Due to the gradual progress of crystallization 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 crystallization. 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 aluminates and gel formation of tetra calcium alumina ferrite.

$$3\ CaO.Al_2O_3 + 6\ H_2O \longrightarrow 3\ CaO.Al_2O_3.6\ H_2O + 880\ KJ/Kg$$

$$C_3A + 6\ H_2O \longrightarrow C_3A.\ 6\ H_2O + 880\ KJ/Kg$$

tricalcium aluminate — hydrated tricalcium aluminate (crystalline)

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

$$C_4AF + 7\ H_2O \longrightarrow C_3A.\ 6\ H_2O + CF.H_2O + 420\ KJ/Kg$$

tetracalcium alumino ferrite — (crystalline) gel

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

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

$$2\ C_2S + 4\ H_2O \longrightarrow C_3S_2.6H_2O + Ca(OH)_2 + 250\ KJ/Kg$$

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

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

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

tricalcium silicate — tobermonite gel — calcium hydroxide (crystalline)

Tri calcium aluminate (C3A) 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 C3A by forming insoluble calcium sulpho aluminate.

Manufacture of Portland Cement: The manufacture procedures of Portland cement is described below.

1. Mixing of raw materials
2. Burning of raw materials
3. Grinding
4. Storage and packaging

1. **Mixing of raw materials**

The major raw materials used in the manufacture of cement are Calcium, Silicon, Iron and Aluminum. These minerals are used in different form as per the availability of the minerals. The following table shows the raw materials for Portland cement manufacture.

Calcareous Materials	Argillaceous Materials		
Calcium	**Silicon**	**Aluminum**	**Iron**
Limestone	Clay	Clay	Clay
Marl	Marl	Shale	Iron ore
Calcite	Sand	Fly ash	Mill scale
Aragonite	Shale	Aluminum ore refuse	Shale
Shale	Fly ash		Blast furnace dust
Sea Shells	Rice hull ash		
Cement kiln dust	Slag		

The mixing procedure of the manufacture of cement is done in two methods, i.e. i) dry process and ii) wet process.

i) Dry process: The both calcareous and argillaceous raw materials are firstly crushed and then grinded to get fine particles into ball. Now these powdered minerals are mixed in required proportion to get dry raw mix which is then stored in silos and kept ready to be sent into rotary kiln. Now the raw materials are mixed in specific proportions so that the average composition of the final product is maintained properly. The flow diagram is given below.

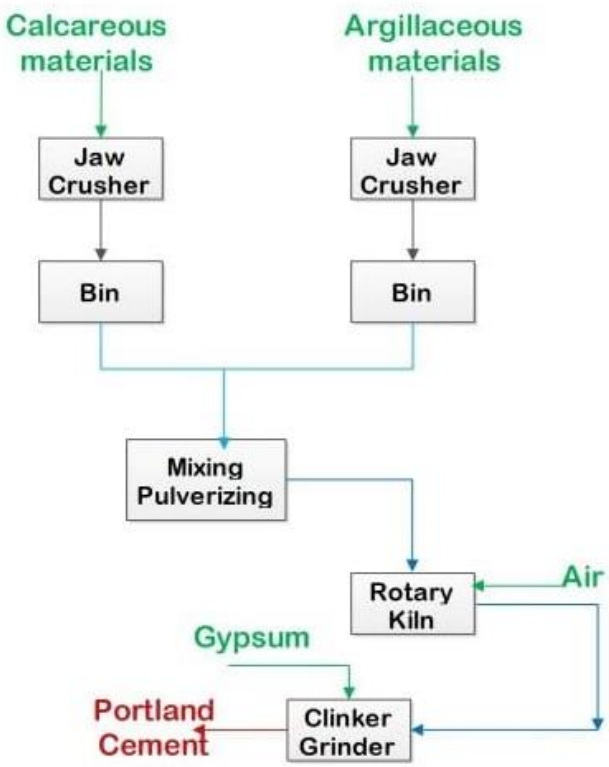

Fig 1: Manufacture of Cement by Dry Process

ii)Wet process: The raw materials are firstly crushed and made into powdered form and stored in silos. The clay is then washed in washing mills to remove adhering organic matters found in clay.

The powdered limestone and water washed clay are sent to flow in the channels and transfer to grinding mills where they are completely mixed to form slurry.

The grinding process can be done in ball or tube mill or even both. Then the slurry is led into collecting basin where composition can be adjusted. The slurry contains around 38-40% water that is stored in storage tanks and kept ready for the rotary kiln.

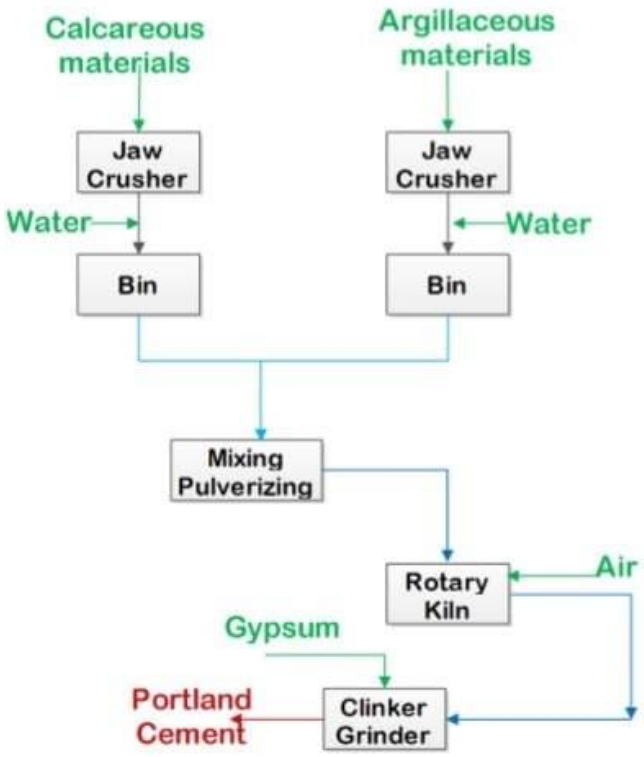

Fig 2: Manufacture of Cement by Wet Process

2. Burning of raw materials:

The burning process is carried out in the rotary kiln which is made up of steel tubes. The inner side of the kiln is lined with refractory bricks. The raw mix of dry process or the slurry of wet process is injected into the kiln from the upper end. The kiln is heated with the help of powdered coal or oil or hot gases from the lower end of the kiln so that the long hot flames is produced. In the upper part of the klin, water or moisture in the material is evaporated at 400 ^{o}C temp, so this process is known as Drying Zone. The central part i.e. calcination zone, the temperature is around 1000 ^{o}C, where decomposition of lime stone takes place. The remaining material is in the form of small lumps known as nodules after the CO_2 is released.

$CaCO_3 = CaO + CO_2$

The lower part (clinkering zone) has temperature in between 1500-1700 ^{o}C where lime and clay are reacts to yielding calcium aluminates and calcium silicates. This aluminates and silicates of calcium fuse to gather to form small and hard stones are known as **clinkers**. The size of the clinker is varies from 5-10mm.

$2CaO + SiO_2 = Ca2SiO_4$ (declaim silicate (C_2S))

$3CaO + SiO_2 = Ca3SiO_5$ (tricalcium silicate (C_3S))

$3CaO + Al_2O_3 = Ca_3Al_2O_6$ (dicalcium aluminate (C_2A))

$4CaO + Al_2O_3 + Fe_2O_3 = Ca_4Al_2Fe_2O_{10}$ (tetracalcium aluminoferrite(C_4AF))

The clinkers coming from the burning zone are very hot. To bring down the temperature of clinkers, air is admitted in counter current direction at the base of the rotary kiln. The cooled clinkers are collected in small trolleys.

3. Grinding of Clinkers:

The cooled clinkers are received from the cooling pans and sent into mills. The clinkers are grinded finely into powder in ball mill or tube mill. Powdered gypsum is added around 2-3% as **retarding agent** during final grinding. The final obtained product is cement that does not settle quickly when comes in contact with water.

After the initial setting time of the cement, the cement becomes stiff and the gypsum retards the dissolution of tri-calcium aluminates by forming tricalcium sulfoaluminate which is insoluble and prevents too early further reactions of setting and hardening.

$3CaO.Al_2O_3 + xCaSO_4.7H_2O = 3CaO.Al_2O_3.xCaSO_4.7H_2O$

4. Storage and Packaging: The grinded cement is stored in silos, from which it is marketed either in container load or 50kg bags.

Question 1: Write down the chemical reactions involved during cement production.

Hints:

- $8C_aO+Al_2O_3.2SiO_2.2H_2O \xrightarrow{1350^\circ} 2\ CaSiO_3+Ca_3(Al_2O_3)_2+2H_2O$
- $2CaO+SiO_2 \rightarrow 2CaO.SiO_2$
- $2CaO+Al_2O_3 \rightarrow 2CaO.Al_2O_3$
- $3CaO+SiO_2 \rightarrow 3CaO.SiO_2$
- $3CaO+Al_2O_3 \rightarrow 3CaO.Al_2O_3$
- $4CaO+Al_2O_3+Fe_2O_3 \rightarrow 4CaO.Al_2O_3.Fe_2O_3$

Question 2: What is retarder? Mention its two functions.

Hints: Chemical agent used to increase the thickening of cement slurries to enable proper placement is known as retarder. Retarders for concrete are used to delay the initial setting time of the concrete upto an hour. Retarders also act as water reducers.

Question 3: What are clinkers?

Hints: During burning process of cement production, the lime and clay are reacts to yielding calcium aluminates and calcium silicates in the lower part of kiln (temperature in between 1500-1700 ^{o}C). This aluminates and silicates of calcium fuse to gather to form small and hard stones are known as **clinkers**. The size of the clinker is varies from 5-10mm.

Question 4: What is the function of Gypsum?

Hints: After cooling, the clinker is pulverized and blended with a small amount of gypsum to control the setting time of the finished cement.

$$C3A + 6H2O \longrightarrow C3A.\ 6H2O + heat$$

After the initial setting, the paste becomes soft and the added gypsum retards the dissolution of C3A by forming insoluble calcium sulpho aluminate.

Question 5: What is white cement?

Hints: White Cement is an ordinary Portland cement in which iron & manganese oxides are added to increase whiteness of cement during manufacturing. Now a days lot of colored cements are available in market which can be manufactured by adding color pigments.

Question 5: What is coloured cement?

Hints: Coloured cements are made by grinding 5 to 10 percent of suitable pigments with white or ordinary gray portland cement. The chromium oxide gives green colour. The cobalt imparts blue colour.

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