ENGINEERING MATERIALS :CEMENT

Contents

Portland Cement; Definition, Manufacturing & Chemistry of setting and hardening of cement.

Cement

Cement is a **binder**, substance that sets and hardens easily, and can bind other materials together.

Cement is a powdered material which initially has plastic flow when mixed with water or other liquid and posses the property of setting into a hard solidstructure in several hours with varying degree of strength and bondingproperties.

History of the origin of cement

In 1824, Joseph Aspdin patented a material, which he called Portland cement, because this powder when mixed with water changed in a hard stone, similar to the prestigious Portland stone found in PORTLAND, England.

Classification of Cement

1. Hydraulic Cement : They are capable of setting and hardening under water. For e.g.Portland Cement.

2.Non- Hydraulic Cement : which harden in air and cannot be used under water. For e.g. Ordinary lime.

Hydraulic Cement is most commonly used and further classified as:

Natural Cement : is made by calcining a naturally occurring argillaceous limestone at high temperature and subsequently, pulverizing the calcined mass. Its setting is quick but has low strength.

Pozzolana Cement : The pozzolana is a volcanic powder. It is found in Italy near vesuvius. It resembles surkhi which is prepared by burning bricks made from ordinary soils. The percentage of pozzolana material should be between 10 to 30.

Slag Cement: Slag cement is a hydraulic cement formed when granulated blast furnace slag is ground to suitable fineness and is used to replace a portion of Portland cement. It is a recovered industrial by-product of an iron blast furnace.

Portland Cement : Portland cement is the most common type of Cement, in general used around the world as a basic ingredient of Building Materials. It is made by calcining the mixture of argillaceous and calcareous raw material (clay and lime containing) at about 1500^0C.

Chemical Composition of Cement

S.N.	Cement Composition	% range (by mass)	Functions
1.	Lime (CaO)	60-70	Too little lime reduces strength, if high it gives early strength but liable for disintegration
2.	Silica (SiO_2)	17-25	Its higher % increases the strength and usually prolongs the setting time.
3.	Alumina (Al_2O_3)	3-8	Its higher percentage increases the strength and reduces the setting time.
4.	Iron Oxide (Fe_2O_3)	2-4	It imparts grey color in cement, impart strength and hardness in cement.
5.	MgO	1-5	Improves the functionality of lime and contribute to the soundness of cement.
6.	SO_3	1-3	It impart soundness to the cement.
7.	Alkali oxide ($NaO+K_2O$)	0.3 -1.5	If present in excess causes the cement efflorescent.

MANUFACTURING OF CEMENT

Portland cement is a mixture of silicates of calcium and aluminium.

Major constituents of cement-

1. Dicalcium silicates($2CaO.SiO_2$)-28%[C_2S]
2. Tricalcium silicates($3CaO.SiO_2$)-46%[C_3S]
3. Tricalcium aluminates($3CaO.Al_2O_3$)-10%[C_3A]
4. Tetra calcium aluminoferrite($4CaO.Al_2O_3.Fe_2O_3$)-9%[C_4AF]
5. Small quantities of CaO and MgO-5%

Raw Material:

Calcareous Materials: These are the source of lime. The following calcareous materials are used:

- Lime Stone (contain $CaCO_3$ 65-80%),
- Chalk
- Shale
- Calcite

Argillaceous Materials: These are the source of silica, iron oxide and alumina. The following argillaceous materials are used:

- Clay
- Sand
- Slate
- Blast Furnace Slag

Manufacturing process-

The complete manufacturing process involve the followingsteps:

- **Crushing**
- **Mixing**
- **Burning**
- **Grinding**
- **Packing**

Above steps/ Manufacturing is carried out bytwo methods:

(A) Dry Process **(B) Wet Process**

In the dry process, the raw materials mixed, fined and then fed into kiln whereasin the wet process, the raw materials are crushed separately and then directly mixed in correct proportion in the presence of water to make a fine thin paste known as Slurry.

Wet Process :

When the raw materials are **soft** , then the wet process is **preferably to be used.** The cement is manufactured by the following procedure:

Mixing of Raw Materials-

- In the wet process, there are two raw materials i.*e.* calcareous and argillaceous. Initially, Calcareous materials are crushed using crushers and Argillaceous material are washed with water in the container.
- After crushing the lime stones are stored in silos similarly after washing the clay is stored in basins.
- The crushed materials from different silos and basins are drawn in correct proportions in a channel called wet grinding mills. **Both the materials are intimately mixed in the presence of water and to form a fine thin paste known as slurry**
- Slurry is then stored in another silo may be called as slurry silo where it is constantly stirred. The composition of raw materials is checked again and, if required, corrected by adding clay or chalk materials as desires.

Burning -

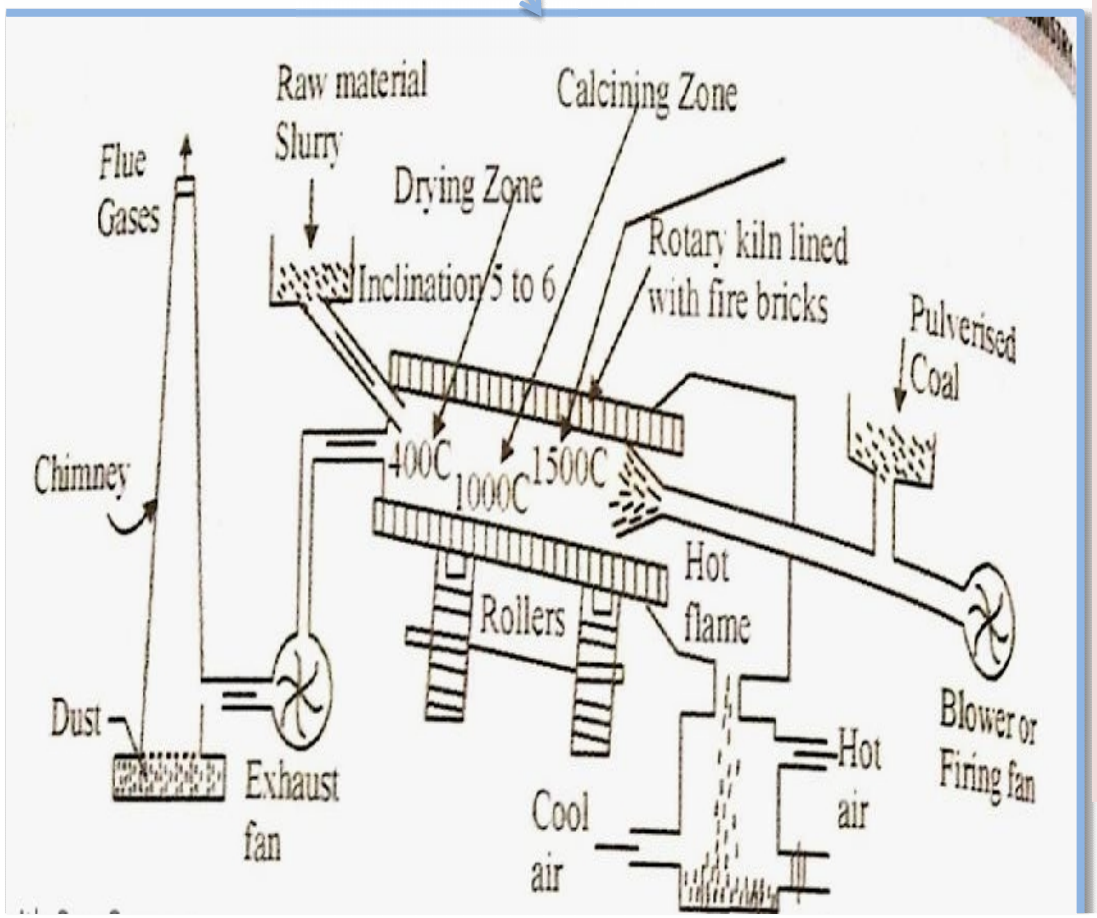
In this operation, the slurry is directly fed into a long inclined steel cylinder called ***Rotary kiln***. Rotary Kiln is a steel tube about 2.5 to 3.0 m in diameter and 90 to 120 min length, lined inside with refractory bricks. The kiln is slightly inclined downward towards the exit and it can be rotated at a desired speed as it is mounted on roller bearings.

There are three different zones in kiln:

Drying Zone (Upper Zone) : In the upper part of kiln, where the temperature is about 400^0C, most of the water in the slurry gets evaporated.

Calcination Zone (Central Zone): The temperature is about 1000^0C, Limestone undergoes decomposition to form quick lime and CO_2 which later escapes out.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$



Burning Zone (Lower Zone) :

The temperature of this zone is around $1500 - 1600^0C$, the mixture melts and forms little rounded pasty mass which is called ***clinkers*** . The main reaction taking place are as follows:

$$2CaO + SiO_2 \longrightarrow Ca_2SiO_4 \text{ (Dicalcium Silicate) } (C_2S)$$

$$3CaO + SiO_2 \longrightarrow Ca_3SiO_5 \text{ (Tricalcium Silicate) } (C_3S)$$

$$3CaO + Al_2O_3 \longrightarrow Ca_3Al_2O_6 \text{ (Tricalcium aluminate) } (C_3A)$$

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow Ca_4Al_2Fe_2O_{10} \text{ (Tetracalcium aluminoferrite) } (C_4AF)$$

Grinding - After cooling the clinkers are carried to the ball mills for grinding. The clinkers are mixed with **2-4% gypsum** during grinding. **The gypsum is used as a retarder, for setting of cement otherwise cement when mixed with warer will set quickly, which is not favorable for the strength of cement.**

Packing: The ground cement is stored in silos, and then packed into bags by automatic packing machines.

S.N.	Dry Process	Wet Process
1.	Process is slow	Comparatively faster
2.	Cement produced is of inferior quality	Cement produced is of superior quality
3.	The process is adopted when raw materials are quite hard.	The process is adopted for any type of raw material.
4.	Fuel consumption is low.	Fuel consumption is higher.

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 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.

Name of the constituent	Chemical formula	%	Setting time
Tricalcium silicate (C_3S)	$3CaO.SiO_2$	45	7 days
Dicalcium silicate (C_2S)	$2CaO.SiO_2$	25	28 days
Tetracalcium aluminoferrite (C_4AF)	$4CaO.Al_2O_3.Fe_2O_3$	9	1 day
Calcium Sulphate (CS)	$CaSO_4$	5	-
Tricalcium aluminate	$3Ca.Al_2O_3$	1	1 day
Calcium oxide	CaO	2	-
Magnesium Oxide	MgO	4	-

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.

$3\ CaO.Al_2O_3 + 6\ H_2O \longrightarrow 3CaO.Al_2O_3.6\ H_2O$; ΔH= - 880 KJ/Kg

$C_3A + 6\ H_2O \longrightarrow C_3A.\ 6\ H_2O$; ΔH= - 880 KJ/Kg

Tricalcium aluminate — Hydrated Tricalcium aluminate (Crystalline)

$4\ CaO.Al_2O_3.Fe_2O_3 + 7\ H_2O \longrightarrow 3\ CaO.Al_2O_3.6\ H_2O + CaO.Fe_2O_3.H_2O$; ΔH= - 420 KJ/Kg

$C_4AF + 7\ H_2O \longrightarrow C_3A.\ 6\ H_2O + CF.H_2O$; ΔH= - 420 KJ/Kg

Tetracalcium alumino ferrite — (crystalline) — gel

Function of Gypsum in Cement

Tri calcium aluminate (C3A) combines with water very rapidly

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

After the initial setting, the paste becomes soft and the added gypsum retards the dissolution of C3A by forming insoluble calcium sulpho aluminate. **(3 CaO.Al2O3.x CaSO4.7 H2O)**

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

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

$2(2\ CaO.SiO_2) + 4\ H_2O \longrightarrow 3\ CaO.2SiO_2.6H2O + Ca(OH)_2$; ΔH= - 250 KJ/Kg

$2\ C_2S + 4\ H_2O \longrightarrow C_3S_2.6H_2O + Ca(OH)_2$; ΔH= - 250 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 silicate.

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

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

tricalcium silicate tobermonite gel calcium hydroxide

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.

Timing & Sequence of chemical reactions during setting & hardening:-