Cement

Cement is defined as inorganic binding material possessing adhesive and cohesive properties and capable of bonding materials like stones, bricks, building blocks, etc.

Portland cement

Cement is named as Portland cement because during setting and hardening of paste cement, the colour and hardness resembles to Portland stone (a type of lime stone).

Portland cement is obtained by heating an intimate mixture of argillaceous (clay containing) and calcareous (lime containing) materials about 1500°C.It is mixed with gypsum. This cement possesses quick setting and hardening property.

Raw materials and functions:

The raw materials required for the manufacture of Portland cement are

(i) Calcareous materials CaO Ex: Limestone, chalk.

(ii) Argillaceous materials, Al_2O_3 and SiO_2 Ex: clay, slate etc

(iii) Powdered coal (or) fuel oil.

(iv) Gypsum ($CaSO_4.2H_2O$)

Manufacture of Portland cement

Manufacture of Portland cement involves the following steps.

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

1. Mixing of raw materials

Mixing of raw materials is done by dry process or by wet process.

(a)Dry Process:

In dry process, the raw materials like limestone and clay (3:1) are crushed, powdered, dried and mixed in definite proportions to get dry mix. It is stored in a concrete storage tank called **silos**.

(b) Wet process:

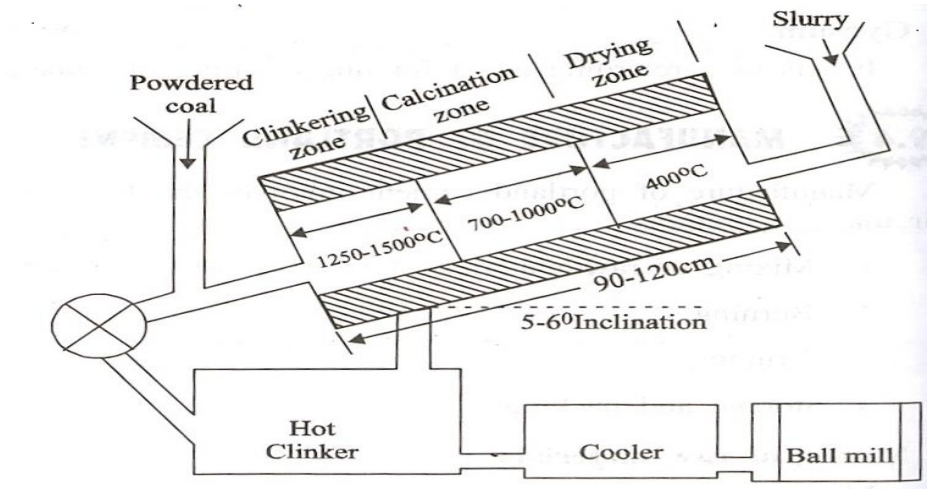
In wet process, the raw materials in definite proportions are finely ground with end to travel slowly to the firing and discharge exit end coated with refractory bricks and capable of

rotating at 1 rpm 9 Revolution per minute). The burning process is usually done in rotary kiln which is a long horizontal steel cylinder

2. Burning

The burning process is usually done in rotary kiln which is a long horizontal steel cylinder(2.5-3.0 m.dia and 90-120 m length) coated with refractory bricks and capable of rotating at 1 rpm (Revolution per minute) .

The rotary kiln is set at a slight inclination of about 5-6°C in order to allow the raw materials fed at one end to travel slowly to the firing and discharge exit end of high temperatures.



Process

The slurry gradually comes down in the kiln into the different zones

1. Drying Zone 400°C
2. Calcination zone 700 -1000° C
3. Clinkering zone 1250-1500°C

(a) Drying Zone:

The upper part of the rotary kiln is known as drying zone, where the temperature is about 400°C. Due to the presence of hot gases in this zone, water is evaporated from the slurry.

(b) Calcinations zone:

The middle part of the rotary kiln is known as calcining zone where the temperature ranges from 700 -1000 C. In this zone lime stone is decomposed into CaO and CO_2.

$CaCO_3 \rightarrow \qquad CaO + CO_2$

Lime stone Quick lime

(c) Clinkering Zone:

The lowest part of the zone is called as clinkering zone, where the temperature is maintained about 1350-1500^{o}C. In this zone lime reacts with clay (Containing Al_2O_3, Fe_2O_3 and SiO_2) and forms aluminates and silicates. The mixture is then finely powdered and fed into the top of the rotary kiln.

$2CaO + SiO_2 \rightarrow 2CaO.SiO_2$ (C_2S)

Di calcium Silicate

$3CaO + SiO_2 \rightarrow 3CaO.SiO_2$ (C_3S)

Tri calcium Silicate

$3CaO + Al_2O_3 \rightarrow 3CaO.Al_2O_3$ (C_3A)

Tri calcium Aluminate

$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow 4CaO.Al_2O_3.Fe_2O_3$($C_4AF$)

Tetra calcium alumino Ferrate

These compounds fuse together to form a hard grayish stone mass called **cement clinkers**. The hot clinker is cooled with atmospheric air and the hot air thus produced is used for drying the coal before grinding.

3. Grinding :

The cooled clinker is then finely pulverized with 2-6% gypsum acts as a retarding agent for quick setting of cement.

4. Storage and Packing:

The cement coming out from the grinding mills is stored in a concrete storage silos. Then the cement is packed in jute bags by automatic machines.

Thus the final setting and hardening of cement is due to the formation of tobermonite gel plus crystallization of $Ca(OH)_2$ and hydrated tricalcium aluminate.

Properties

1. Setting and Hardening of cement:

When the cement is mixed with water, hydration and hydrolysis of cement begin, resulting in the formation of gel and crystalline products. The insoluble gels and crystals have the ability to surround inert materials like sand, bricks, crushed stones etc

Setting:

It is defined as the stiffening of the original plastic mass, due to the formation of tobermonite gel.

Hardening:

It is defined as the development of strength, due to formation of crystals.

Chemical reactions involved in setting and hardening of cement:

(i).When water is mixed with cement , hydration of tricalcium aluminate (C_3A)occurs rapidly and the paste becomes quite hard within a short time known as initial set are flash set.

$3CaO.Al_2O_3 + 6H_2O$-------$3CaO.Al_2O_3.6H_2O$

Tricalcium aluminate Hydrated tricalcium aluminates(crysatalline)

$C_3A + 6H_2O$ -----→ $C_3A.6H_2O$

Role of gypsum in cement:

In order to retard the rapid hydration of C_3A, gypsum is added during grinding of cement clinkers.

Gypsum reacts with C_3A to form insoluble calcium sulphoaluminate complex, which does not possess hydrating property and retards early setting of cement.

$C_3A + 3CaSO_4.2H_2O$--------$C_3A.3CaSO_4.2H_2O$

(ii)After the hydration of C_3A, C_3S begins to hydrate to give tobermonite gel and crystalline $Ca(OH)_2$. The hydration of C_3S takes place within 7days.It does not contribute much to the strength of the cement.

$2(3CaO.SiO_2) + 6H_2O$--------- $3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$ + 500kj/kg

(or)

$2C_3S + 6H_2O$ -------→ $C_3S_2.3H_2O + 3Ca(OH)_2$

Tobermonite gel has very high surface area and very high adhesive property.

(iii) Dicalcium silicate reacts with water slowly and gets finished 7-28days.

$2(2CaO.SiO_2) + 4\ H_2O$ --------$3CaO.2SiO_2.3H_2O + Ca(OH)_2$ + 250kj/kg

The increase in strength takes place due to the formation of tobermonite gel and crystalline $Ca(OH)_2$ of the both C_2S and C_3S.

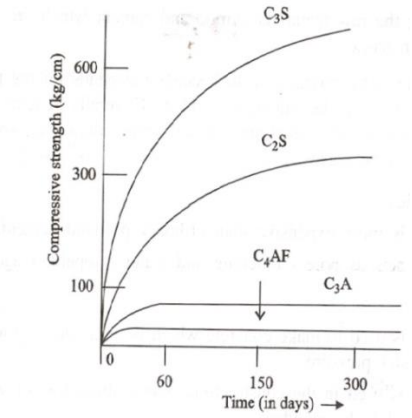
(iv)Hydration of tetra calcium aluminoferrite takes place initially; the hardening takes place finally through crystallization along with C_2S.

$4CaO.Al_2O_3.Fe_2O_3 + 7H_2O$----------$3CaO.Al_2O_3.6H_2O + CaO.Fe_2O_3.H_2O$ + 420KJ

Crystalline gel

The final setting and hardening of cement is due to the formation of tobermonite gel plus crystallization of $Ca(OH)_2$ and hydrated tricalcium aluminate.

Development of compressive strength of the cemnt, due to hydration and hydrolysis of bogue compounds shown in graph.



2. Heat of hydration

When water is mixed with portland cement some amount of heat is liberated due to the hydration and hydrolysis reactions of Bogue materials. The heat of hydration of the compounds are in the following order.

C3A > C3S >C4AF >C2S

800 500 420 250 kj/kg

The average quantity of heat liberated is 500kj/kg.The heat generated during hydration of cement must be dissipated as quick as possible to avoid crack formation on setting and hardening.