Cement

Cement:-

The powdery form of calcareous & Argillaceous material in the required comp which can form, the concrete by mixing rocks, sand and water is known as cement. For e.g. portland cement, hydraulic cement etc.

Manufacture of cement:

(1) Raw materials

Raw materials used in manufacture of portland cement are:-

(a) calcareous Material (which supply lime) e.g limestone, chalk, Marl or marine shells, $CaCO_3$ & less than 5% MgO.

(b) Argillaceous material (which supply silica, alumina & iron oxide) eg:- clay or shale, blast-furnace, ashes & cement rock.

(2) Manufacture of cement clinker:

(a) The lime saturation factor, $\frac{CaO}{2.8SiO_2 + 2Al_2O_3 + Fe_2O_3}$

Should be in the range of 0.66 - 1.02. This will ensure formation of C_3S, C_2S, C_3A (Tricalcium Silicate, dicalcium Silicate, tricalcium aluminate).

(b) Silica modulus $\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$ should be 2.2 to 3.5

The req ratio of lime and silica grined and MgO should be bellow the specified limits and also alkali choring with in the specified limits.

(3) Methods of Manufacturing :-

Portland of cement is generally manufacture by the following 3 method

Wet Process :-

In this process the req raw materials are brought into the flowing slurry which contain 30-40% water. The slurry was transfered into rotatary kiln (furnance) in which the raw material was grined into powder form to 400°c, where it losed all water. After then, the powder was transfered into middle portion of kiln where 900-1000°c temp was maintained, the lime stone decomposed to form CaO and CO_2. Then, powder form was transferred into lower portion of rotatary kiln where 1400-1600°c temp was maintained and limes & clay combines to form calcium silicates and aluminates.

$CaCO_3 + Al_2O_3 + Fe_2O_3 + SiO_2 + H_2O \longrightarrow 2CaO \cdot SiO_2$

$3CaO \cdot SiO_2, 3CaO \cdot SiO_2$

$3CaO \cdot Al_2O_3$

$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

C_2S ⟶ Dicalcium silicate
C_3S ⟶ tricalcium silicate
C_3A ⟶ Tricalcium aluminate
C_4AF ⟶ Tetracalcium alumino-ferrite

The resulting product is known as clinker which is in the form of small balls or pellets of varying size. The clinker are cooled in rotatory cooler and mixed with 2-3% gypsum and kept in a grinding machine. The resulting powder is known as portland cement.

Dry Method :-

In this process, the calcareous and argillaceous materials are crushed in gyrator crushers. dried and mixed, pulverised and homogenised with the help of compressed air. This 'raw meal' is introduced into the upper end of the rotary kiln while a blast of burning coal dust is blown from the other end. The rxn taking place and place and rest of the process is same as described under wet process.

Semi-dry process :-

In this process, the raw materials are initially ground dry, but instead of feeding as a powder the 'raw meal' is moduliised with 10-14%. Water in a pan or

drum type noduliser. The nodules are fed on a travelling grate where they get dried and preheated before entering a short rotary kiln where they are burnt to form cement clinker.

Setting & hardening cement:

According to the colloidal theory of michaelis, hardening of cement is due to the interlocking of the crystalice ~~is due to the interlocking of the~~ products formed during hydration of the constitutional compounds. It is generally agreed that setting and hardening of cement are essentially due to the formation of interlocking crystals reinforced by the rigid gel formed by the hydration and the hydrolysis of constitutional compounds.

When cement is mixed with water the paste becomes quit rigid with in a short time which is known as initial set. This is due to C_3A which hydrate rapaidly as follow:

$$3CaO \cdot Al_2O_3 + 6H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O$$
(crystals)

However the crystal prevents the hydration rxn of other constitutional compound formind barrier over them so, gypsum

($CaSO_4 \cdot 2H_2O$) or, plaster of paris was mixed for hydration rxn.

$3CaO \cdot Al_2O_3 \cdot xH_2O + xCaSO_4 \cdot 2H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot \frac{x}{2} H_2O$

The tetracalcium aluminoferrite (C_4AF) then reacts with water forming both gels and crystaline compound.

$4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 7H_2O \xrightarrow{C_4AF} 3CaO \cdot Al_2O_3 \cdot 6H_2O + CaO \cdot Fe_2O_3 \cdot H_2O$
crystals

These gels shrinks with passes of time and leave some capillaries for water to come & contact with C_3S & C_2S to undergo further hydration & hydrolysis rxn.

$CaO \cdot SiO_2 + xH_2O \xrightarrow{C_3A} \underset{\text{gel}}{2CaO \cdot SiO_2} (x-1)H_2O + Ca(OH)_2$ crystal

$CaO \cdot SiO_2 + xH_2O \xrightarrow{C_2A} 2CaO \cdot SiO_2 \cdot xH_2O$
gel

The setting and hardening of cement maybe summarized diagramatically as follow

Unhydrated cement
- hydration → Metastable gel → stable gel → crystalline products
- hydration → crystalline hydration products