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Cement:

The term cement is used for materials possessing adhesive and cohesive properties, which make them capable of binding mineral fragment like bricks, stones, tiles etc in to a compact coherent structure. Cement have the property to form a paste with water and setting in to a hard solid mass in few hours.

Depeding upon the property of hardening in air or water cement can be classified as -

(i) **Hydraulic cements:** Cements capable of hardening and setting because of hydration and hydrolysis reaction between the anhydrous cement powder and water.

Example: Portland cement

(ii) **Non- Hydraulic cements:** Cement that harden in air and cannot be used under water. Example: slaked limes (calcium hydroxide mixed with water), harden due to the carbonation reaction by carbon di oxide present naturally in the air.

Classification of cement: Hydraulic cements are mostly used and are classified as follows

(a) Natural Cement: The natural cement made by calcining naturally occurring lime stone 9called as argillaceous limestone contains 20-40% clay) at high temperature and the calcined mass was crushed in to powder. During the calcination silica and alumina present in the clay combine with lime to form corresponding calcium silicates and alluminates.

Properties:

(i) Natural cement possess Hydraulic properties

(ii) It is quick setting cement but they have low strength

(iii) Mortar made from natural cement and sand is used in laying bricks and steeing stones

Uses: Used in lage masses of concrete such as dams and foundations.

Puzzolana cement: Puzzolana are the deposit of volcanic ash produced by the rapid cooling of lava (mixture of silicates of Ca. Fe and Al). When Puzzolana are mixed with slaked lime without the use of heat it form hard mass in presence of water to give hydraulic cement.

Uses: Puzzolana cements are used by Greeks and Romans in the form of Mortar.

(Mortar: A mixture of lime . sand and water)

Slag Cement: Slag cement is obtained by mixing blast furnace slag (alluminium silicate) and hydrated lime then the mixture is poured into cold water. The granular cement produces is dried and mixed with lime. The mixture is then pulverized to fine powder. Slag cement are slow setting cements. They can harden by adding accelerators such as clay, salt or caustic soda. The strength of slag cement is very poor. It is mainly used for making concrete for construction in waterlogged area where the tensile strength is less important.

Portland cement: Portland cement is made by the calculated amount of clay containing and lime containing materials followed by gypsum for retarding calcination. *It is defined as "an extremely finely grounded product obtained by calcination together at about 1500⁰C, an intimate and proportioned mixture of argillaceous (clay containing) and calcareous (lime containing) raw materials, without the addition of anything subsequent to calcination, excepting the retarder gypsum."* The setting and hardening properties of this type of cement resembles with Portland rock, so it is named as Portland cement. It is a mixture calcium silicates and aluminates with small amount of gypsum. All the Portland cement are hydraulic in nature, which are capable of setting and hardening under water by the interaction of water with the constituents of cement.

Composition, properties and uses of special cement:

(1) High alumina cement: High alumina cements are made by fusing a mixture of bauxite and lime stone at ~ 1500- 1600⁰C in rotary kiln and grinding resulting mass in to fine powders.

(i) Composition: 35- 40% CaO ; 35-55% Al_2O_3; 5 – 15% FeO +Fe_2O_3 ; and 5- 10% SiO_2.

The most important constituent of such cements constituent of such cements are monocalcium aluminate (CA) and tricalcium pentaaluminate (C_3A_5). Besides some dicalcium silicate (C_2S) and tetracalcium aluminoferrite (C_4AF) are also constituent of high alumina cement. Both CA and C_3A_5 hydrate initially to get gel which has chemical formula $CaAl(OH)_5 . 3H_2O$.

(ii) Properties:

(a) Compare to Portland cement the rate of hardening of high alumina cement is very high and full strength is attain within 24 hours.

(b) Since crystalline complexes such as CA, C_3A_5 *etc* formed from high alumina cements are very stable which make retains their strength even at high temperature.

(c) As compared to Portland cement it has higher chemical resistance to sea water and sulphate bearing ground water. Such cement is resistant to very dilute acid solutions and dilute sulphurous acid solution and to H_2S solution. Therefore it is widely used in chemical industries.

(d) It is not suitable for mass construction as it's evolve high amount of heat of hydration within a short period of time hence increases temperature of concrete mass. So high alumina used for concrete formation under freezing condition.

(e) Ordinary Portland cement shouldn't be mixed with high alumina cement, rather these two should not come in contact with each other, since "Flash set" may occur.

(iii) Application: High alumina cement is used for making refractory concrete to withstand high temperature along with heat resistant property. It is also used in fire pipes construction of electric furnaces, kilns *etc.*

(2) White Portland cement: White Portland cement similar to ordinary, gray Portland cement in all aspects except for its high degree of whiteness. The whiteness occurs due to absence of coloring agent like iron oxide. Obtaining this color requires substantial modification to the method of manufacture, and because of this, it is somewhat more expensive than the gray product. The raw materials for white Portland cement could be white chalk or lime stone and china clay (kaolinite) and the manufacturing process also controlled so that the colouring oxide do not enter in to the clinker.

Composition: Presence of sufficient amount of colorless constituent dicalcium silicate (C_2S. ~ 60%), tricalcium silicate (C_3S, ~20-30 %), and tricalcium alluminate (C_3A, ~ 10%) etc along with absence of Iron oxide are responsible for whiteness of particular cement.

Properties: The mechanical properties of both white and grey Portland cement are almost similar but strength of white Portland cement is higher than grey Portland cement.

Applications: It is used for repairing and joining marble pillars, manufacture of tiles and for mosaic works. For the mosaic works cements may be coloured by means of colouring agent like yellow ochre, venetian red etc.

(3) Sorel cement: Sorel cement (also known as magnesia cement) is a non-hydraulic cement. It is made by the addition of a strong solution of magnesium chloride to finely powdered magnesia.

Composition: Sorel cement sometimes known as magnesium oxychloride cement [$3MgO. MgCl_2. 11H_2O$]. It sets hard in three to four hours.

Applications: Sorel cement is used in composite flooring. Such flooring have the advantage of being non-slip, fire-proof, not easily stretchable, durable and capable of taking a good wax or oil polish.

(4) Barium and strontium cements: Barium and strontium cements are obtained by partial or complete replacement of calcium ions in the calcium silicate and calcium alluminate by Barium and strontium ions. Both Ba^{2+} and Sr^{2+} silicates are more reactive than dicalcium silicates and rate of hydration of these phases higher than dicalcium silicates. Such cements show increased resistant to penetration by radioactive radiations. So these are used in concrete shields for atomic piles.

(5) Silicates cements or acid resistant cements: Silicates cements or acid resistant cements are produced by mixing an inert acid-resisting aggregate such as finely grounded quartz with sodium or potassium or silicate ester in suitable proportion. Their cementing properties due to silica gel and suitable additive like sodium Fluosilicates (Na_2SiF_6) or ethyl acetate or by evaporation of water. Na_2SiF_6 accelerates the hardening and increase the resistance of cement to acid. The binding material of acid resistant cement is soluble glass which is water solution of sodium silicate ($Na_2O.nSiO_2$) or potassium silicate ($K_2O.nSiO_2$) where *n* is the glass modulus.The bond developed by silicates cements is hard but also brittle. On drying cement becomes very porous and permeable to liquids. For this reason it should always kept wet or immersed in a liquid to prevent shrinking of the gel. The **acid-resistant cement** is used for acid-resistant and heat-resistant coatings for setting up of chemical industry.

(6) Water proof cement: Is a cement obtained by adding water proofing substances like calcium stearate, aluminium stearate and gypsum with tannic acid to ordinary Portland cement

Properties:

(a) More expensive than ordinary Portland cement

(b) Acts as pore – blocking and water – repelling agent. Chemically inactive substance like calcium soaps, aluminium soaps, resin, vegetable oils, waxes coal-tar residue etc added as pore blocking agents. These acts as water repelling agents.

Applications:

(i) Used to make concrete which is waterproof under pressure

(ii) Used in construction, where absorption of water need to be avoided

(iii) Used in construction of bridges and under water constructions

Manufacture of Portland cement:

Portland cement is manufactured by mixing lime and clay. The raw materials used for the manufacture of Portland cement are given bellow.

(i) Calcareous materials: These materials supply lime, lime stone, chalk, calcite, waste calcium carbonate from industrial process. These materials contains 3-4% SiO_2, Al_2O_3, and 3% MgO.

(ii) Argillaceous materials: These materails supply silica, iron oxide and alumina such as clay, marl, shale etc. These materials 2.5 to 4 times more silica than alumina.

(iii) Gypsum ($CaSO_4.2H_2O$): Increases initial setting of cement.

(iv) Powdered coal: It is used for burning purpose.

The manufacture of Portland cement involves the mixing of calcareous and argillaceous substances in the required ratio. The small amount of variation of these materials changes the property of cement.

eg.

Lime: Lesser amount of lime makes cement for quick setting but reduces the strength of cement. Whereas high higher amount of cement is responsible for expand and disintegrate of cement.

Silica: Imparts the strength of cement.

Alumina: Make the cement for quick setting but presence of excess alumina weaken the strength of cement.

The various process involved in the manufacture of cement are

(i) Mixing, (ii)Burning, (iii) Cooling, (iv) Grinding and (v) Packing.

(i) Mixing of raw materials: The finely powder raw materials are mixed either by (a) dry process or (b) wet process.

Dry Process: This process is used when raw materials quite hard. In this process the raw materials are grind separately without adding water. In this process lime stone and clay (or shale) with roughly size 2-5 cm used as raw materials. Then these fine powder stored in hoper and mixed with the required proportion such a way that composition of final product is lime (~ 60-69%), silica (~ 17-25%), alumina (~ 3-8%) and Fe_2O_3 (~ 2-4%) to get dry "raw mix". The "raw mix" materials stored in storage bins known as "Silos" and kept ready to be fed into rotary "kiln".

Composition of Raw mix in dry process:

Component	*Percentage range by mass*
Lime (CaO)	60–69
Silica (SiO_2)	17–25
Alumina (Al_2O_3)	3–8
Iron oxide (Fe_2O_3)	2–4
Magnesium oxide (MgO)	1–5
Sulphur trioxide (SO_3)	1–3
Alkali oxides ($Na_2O + K_2O$)	0.3–1.5

Wet Process: In this process the raw materials are crushed, powdered and stored in "silos". In this process mixed with is grinded to particles with suitable size whereas argillaceous materials (clay) is thoroughly washed with water to remove organic matter. Both lime stone and washed wet-clay materials mixed together to form slurry by using water such way that slurry contains 38-40% of water.

(ii) Burning: The grinding mixture of raw materials obtained by dry process or wet process is brunt in a rotary kiln to make clinkers. The chemical reactions which takes place in the kiln are as under.

(a) Drying zone: This is the upper one fourth portion of the kiln where the temperature is 100-500^{0}C. This zone is known as drying zone because all the moisture from the slurry removed here. The dry materials moves down the kiln.

(b) Calcination zone: It is the middle part of the kiln. The temperature of kiln here is ~ 1000^{0}C. All the organic matter present in raw materials burnt here and calcium carbonate decomposes to from CaO and CO_2.

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

(c) Burning zone or clinkering zone: It is the hottest and lower most portion of the kiln. The temperature here is 1400-1600^{0}C. In this zone mixture melts and there is chemical reaction occurs between lime and clay to form calcium aluminates and silicates. The reaction taking place are given bellow.

$$2\,CaO + SiO_2 \longrightarrow \underset{\text{Dicalcium silicate } (C_2S)}{Ca_2SiO_4}$$

$$3\,CaO + SiO_2 \longrightarrow \underset{\text{Tricalcium silicate } (C_3S)}{Ca_3SiO_5}$$

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

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

The calcium aluminates and silicates combine together to from small round greyish stone which is known clinkers.

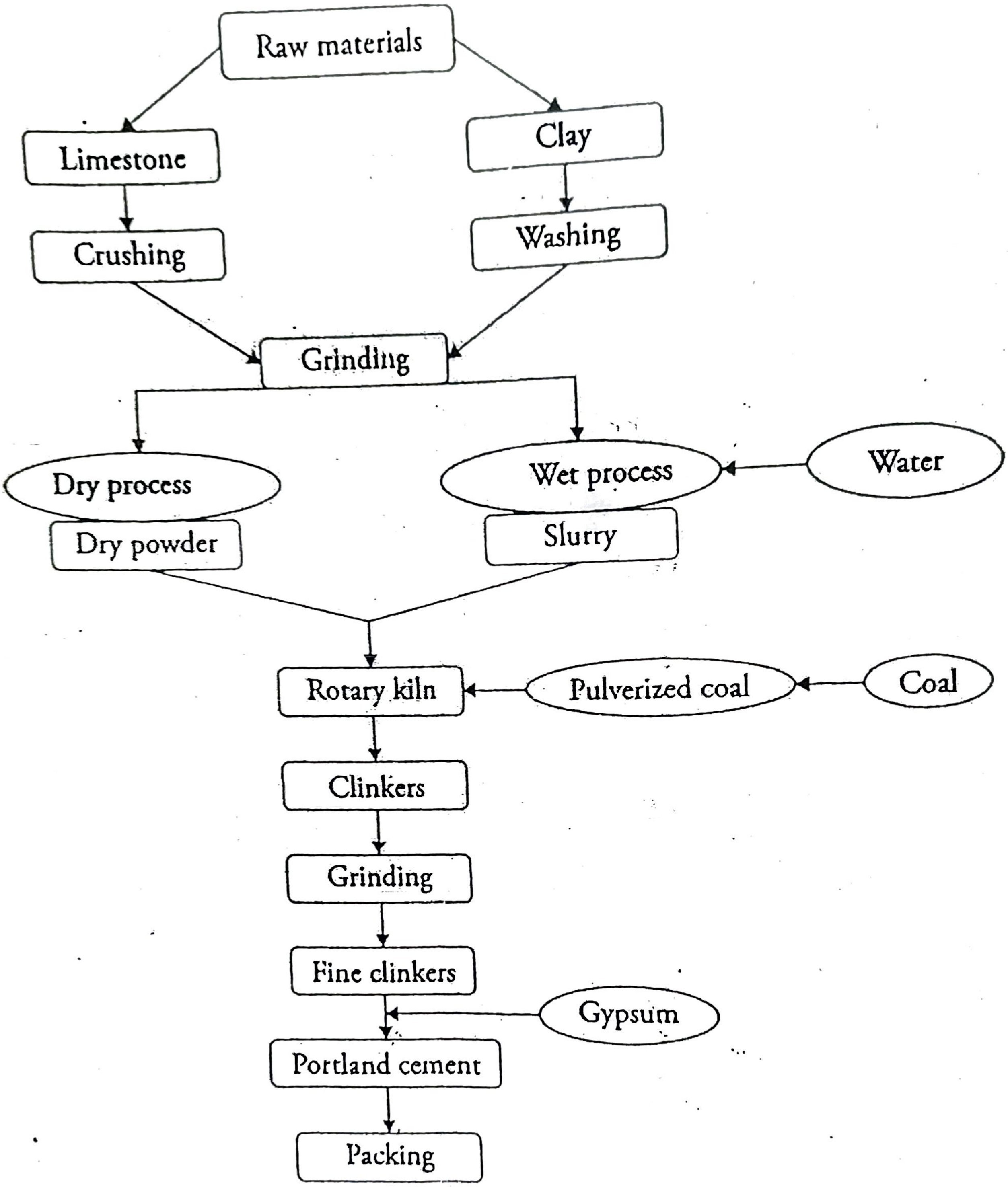
(iii) Cooling zone: The clinkers produce by above procedure are cooled by a stream of air. It is an important process in order to produce a definite degree of crystallization of the melted clinkers.

(iv) Grinding: The cooled clinkers are grounded in ball mill with the addition of 2-5 % of gypsum. The finely grounded clinkers set very quickly when they comes contact with water.

Gypsum ($CaSO_4.2H_2O$) acts as a retarding agent and delay this setting. When cement is mixed with water, the intial sets take place due to hydration of tricalcium alluminate . Gypsum reacts with tricalcium alluminate and forming insoluble tricalcium sulphoalluminate which does not hydrate quickly.

$$\underset{\text{After initial set}}{3\,CaO\,.\,Al_2O_3} + \underset{\text{Gypsum}}{x\,CaSO_4\,.\,7\,H_2O} \longrightarrow \underset{\substack{\text{Tricalcium sulphoaluminate} \\ (\textit{Insoluble})}}{3\,CaO\,.\,Al_2O_3\,.\,x\,CaSO_4\,.\,7\,H_2O}$$

(v) Packing and supply: The cement coming out of the grinding mill is stored in concrete storage called silos. Moisture free air is used to agitate the cement and keep it free from compaction. The cement is packed in bag by automatic packing machine with weight ~50kg/bag.



Flow chart for the manufacture of cement by rotary kiln process.

CHEMICAL CONSTITUTION OF PORTLAND CEMENT

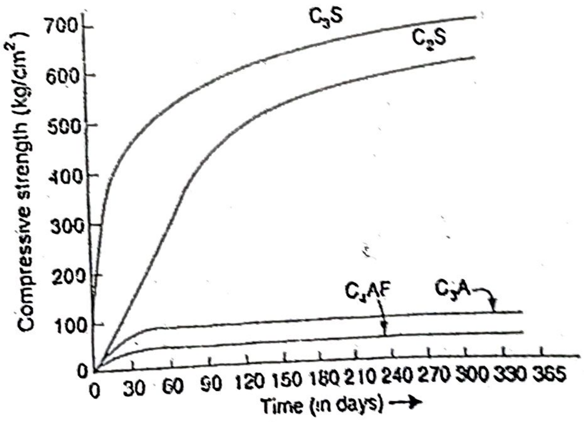
Average compound composition of Portland cement is :

Name of compound	*Chemical formula*	*Abbreviation used*	*Average %*	*Setting time*
Tricalcium silicate	$3CaO \cdot SiO_2$	C_3S	45	7 days
Dicalcium silicate	$2CaO \cdot SiO_2$	C_2S	25	28 days
Tricalcium aluminate	$3CaO \cdot Al_2O_3$	C_3A	1	1 day
Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	9	1 day
Calcium sulphate	$CaSO_4$	-	5	-
Calcium oxide (*free*)	CaO	-	2	-
Magnesium oxide	MgO	-	4	-

Characteristics of constituents : (*i*) *Tricalcium silicate* (C_3S) has "*medium*" rate of hydration ; and *develops high ultimate strength quite rapidly*. Moreover, its ultimate-strength is also the *highest* amongst all the constituents. So it is responsible for ultimate-strength. The heat of hydration is about ~~880 kJ/kg~~. 500 KJ/Kg

(*ii*) *Dicalcium silicate* (C_2S) has quite low early-strength, but develops ultimate-strength of *slightly less than* that of C_3S. It hydrates *very slowly*. It is also responsible for ultimate-strength. It possesses the heat of hydration of ~~420 kJ/kg~~. 250 KJ/Kg

(*iii*) *Tricalcium aluminate* (C_3A) hydrates slowly and *does not* contribute much to the strength of cement, since its early-strength and ultimate-strength are *poorest* amongst all the constituents. Its heat of hydration is about ~~250 kJ/kg~~. 880 KJ/Kg



Development of strength by major constituents in cement.

Setting and hardening of cement:

When cement is mixed with water and allowed to stand in changes to a hard rigid mass. This is known as setting. Setting refers to a change from a fluid state to a rigid state due to initial gel formation. Setting can be defined as stiffening of the original plastic mass due to initial gel formation and chemical reaction. Gradually, the rigid mass gains strength to form a compact rock-like materials known as hardening. Hardening is development of strength due to crystallization.

Setting and hardening takes place due to hydration and hydrolysis reaction of various constituent of cement. The hydrated compound being less soluble, precipitate out as gel or crystals. These insoluble gel surrounded inert materials like sand and crushing stones and bind them strongly. It is believe that hardening takes place due to interlocking of the crystalline products formed during hydration.

Setting occurs within 24 hours, whereas hardening requires 15 to 30 days. It is believe that the setting times of tricalcium alluminate (C_3A), tetracalcium aluminoferrite (C_4AF) tricalcium silicate (C_3S) and dicalcium silicate (C_2S) are 1 day, 1 day, 7 days and 28 days respectively.

Cement + Water Paste $\xrightarrow{1^{st}\text{ day}}$ Hydration of C_3A and C_4F $\xrightarrow{7^{th}\text{ day}}$ Gelation of C_3S $\xrightarrow{28^{th}\text{ day}}$ Gelation of C_2S and C_3S

Setting is the stiffening of original plastic mass due to the formation of tobermonite gel". It can be divided into 2 stages a) Initial Set b)Final Set

Initial setting: When cement is mixed with water, the paste becomes rigid within a short time which is known as initial setting or Flash setting.This is due to the hydration of tricalcium aluminate and gel formation of tetra calcium alumino ferrite. The hydration of tricalcium aluminate (C3A) takes place within a day.

$$3CaO . Al_2O_3 + 6H_2O \longrightarrow 3CaO . Al_2O_3 . 6H_2O + 880 \text{ kJ/Kg}$$

Tricalciumaluminate — Hyderated tricalcium aluminate (Crystalline)

[OR]

$$C_3A + 6H_2O \longrightarrow C_3A . 6H_2O \quad + 880 \text{ kJ/Kg}$$

Tricalcium aluminate (C_3A) combines with water very rapidly with the evolution of large amount of heat. Flash set is not desirable at it causes loss of workability of cement and prevents hydration of other constituent of cement. Adding gypsum retards the dissolution of C_3A by forming *insoluble Tricalcium sulpho-aluminate.*

$$3CaO . Al_2O_3 + xH_2O + yCaSO_4 . 2H_2O \longrightarrow 3CaO . Al_2O_3 . yCaSO_4 + zH_2O$$

Where z = 7-32 H_2O

b) Tetracalcium aluminoferrite also undergoes hydrolysis forming crystalline products.

$$4CaO. Al_2O_3.Fe_2O_3 + 7 H_2O \rightarrow 3CaO.Al_2O_3.6 H_2O + CaO. Fe_2O_3. H_2O + 420 \text{ kJ/kg}$$

$$\underset{\text{Tetracalcium aluminoferrite}}{C_4AF} + 7 H_2O \rightarrow \underset{\text{(Crystals)}}{C_3A .6 H_2O} + \underset{\text{(Gel)}}{CF. H_2O} + 420 \text{ kJ/kg}$$

(c) **Days 2-7**

After hydration of C_3A, C_3S beings to hydrate to give tobermonitegel and crystalline $Ca(OH)_2$,which is responsible for initial strength of the cement. The hydration of C_3S gets completed within 7 days.

$$\underset{\text{Tricalcium silicate}}{2[3CaO.SiO_2]} + 6H_2O \longrightarrow \underset{\text{Tobermonite gel}}{3CaO.2SiO_2 . 3H_2O} + \underset{\text{Crystalline}}{3Ca(OH)_2} + 500\ kJ/Kg$$

[OR]

$$2C_3S + 6H_2O \longrightarrow \underset{\text{Tobermonite gel}}{C_3S_2 . 3H_2O} + 3Ca(OH)_2 + 500\ kJ/Kg$$

Tobermonite gel possesses a very high surface area and very high adhesive property

(d) **Final setting and hardening:**

Day – 7 to 28 :

- Dicalcium silicate (C_2S) reacts with water very slowly and gets completed in 7 to 28 days

$$\underset{\text{Dicalcium silicate}}{2[2CaO . SiO_2]} + 4H_2O \longrightarrow \underset{\text{Tobermonite gel}}{3CaO .2SiO_2 . 3H_2O} + \underset{\text{Crystalline}}{Ca(OH)_2} + 250\ kJ/Kg$$

[OR]

$$2C_2S + 4H_2O \longrightarrow C_3S_2 . 3H_2O + Ca(OH)_2 + 250\ kJ/Kg$$

Increase of strength is due to formation of tobermonite gel and crystalling $Ca(OH)_2$ of both C_2S and C_3S

Function of gypsum in cement: Tricalcium aluminate (C_3A) combines with water very rapidly with the evolution of large amount of heat. Flash set is not desirable at it causes loss of workability of cement and prevents hydration of other constituent of cement. Adding gypsum retards the dissolution of C_3A by forming *insoluble Tricalcium sulpho-aluminate.*

$$\underset{\text{Tricalciumaluminate}}{3CaO \cdot Al_2O_3 + 6H_2O} \longrightarrow \underset{\text{Hyderated tricalcium aluminate (Crystalline)}}{3CaO \cdot Al_2O_3 \cdot 6H_2O} + 880\ kJ/Kg$$

[OR]

$$C_3A + 6H_2O \longrightarrow C_3A \cdot 6H_2O + 880\ kJ/Kg$$

$$3CaO \cdot Al_2O_3 + xH_2O + yCaSO_4 \cdot 2H_2O \longrightarrow 3CaO \cdot Al_2O_3\ yCaSO_4 + zH_2O$$

Where z = 7-32 H_2O

The setting and hardening of cement