

Cement:

A cement is a binder, a substance that sets and hardens and can bind other materials together. Its principal constituents for constructional purpose are compounds of Ca (calcareous) and Al + Si (argillaceous). So the term cement is used for materials possessing adhesive and cohesive properties, which make them capable of binding mineral fragments like bricks, stones, tiles etc. into a compact coherent structure. Cement has the property to form a paste with water and setting into a hard solid mass in a few hours.

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

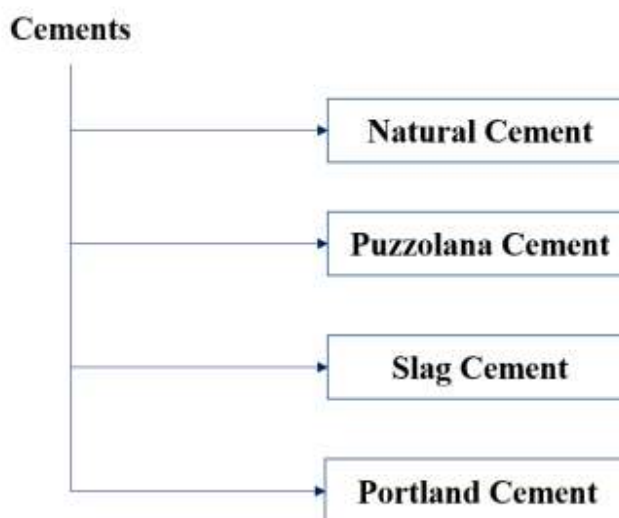
(i) **Hydraulic cements:** Cements capable of hardening and setting because of hydration and hydrolysis reaction between the anhydrous cement powder and water. So the cements which have the property of setting and hardening under water, by virtue of certain chemical reaction with it and are called 'hydraulic cements'.

Example: Portland cement

(ii) **Non- Hydraulic cements:** Cement that hardens in air and cannot be used under water.

Example: slaked limes (calcium hydroxide mixed with water), harden due to the carbonation reaction by carbon dioxide present naturally in the air.

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



(a) Natural Cement: The natural cement made by calcining naturally occurring lime stone (called 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 aluminates.

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 large 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 forms 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 are 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.

CHEMICAL CONSTITUTION OF PORTLAND CEMENT

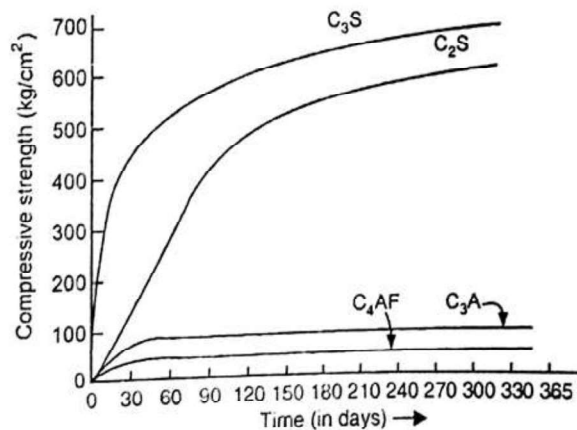
Average compound composition of Portland cement is :

Name of compound	Chemical formula	Abbreviation used	Average %	Setting time
Tricalcium silicate	$3\text{CaO} \cdot \text{SiO}_2$	C_3S	45	7 days
Dicalcium silicate	$2\text{CaO} \cdot \text{SiO}_2$	C_2S	25	28 days
Tricalcium aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	C_3A	1	1 day
Tetracalcium aluminoferrite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	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.

(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.

(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.



Development of strength by major constituents in cement.

Manufacture of Portland cement:

1, Raw materials of Portland Cement and it's use

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 .

Functions:

- Principal Constituent and its proportion can be regulated
- Excess of lime reduces the strength and makes the cement expand & disintegrate
- Lesser amount of lime also reduces the strength by quick setting

(ii) Argillaceous materials: Mainly Al_2O_3 and SiO_2 [eg. Clay]

These materials supply silica, iron oxide and alumina such as clay, marl, shale etc. These materials 2.5 to 4 times more silica than alumina.

Functions:

- Imparts strength
- Makes quick setting
- Excess of alumina weakens the cement

(iii) Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$): 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 weakens the strength of cement.

2. The various process involved in the manufacture of cement are

(i) Mixing

(ii) Burning

(iii) Cooling

(iv) Grinding

(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 hopper 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:

<i>Component</i>	<i>Percentage range by mass</i>
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 ($\text{Na}_2\text{O} + \text{K}_2\text{O}$)	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.

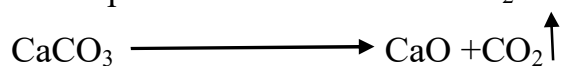
(ii) Burning:

Process: The “raw-mix” is injected into the kiln and its upper end; while hot flames is forced into the kiln from the lower end. Due to slope and slow rotation of the kiln, the materials fed in move continuously towards the hottest-end at a speed of about 15 m per hour. As the mixture of slurry gradually descends, the temperatures rise.

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.

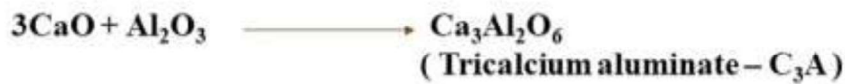
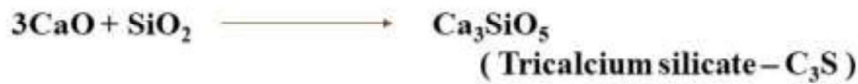
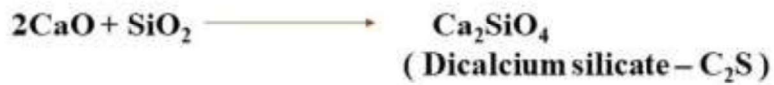
(a) Drying zone: This is the upper one fourth portion of the kiln where the temperature is 100-500⁰C. This zone is known as drying zone because all the moisture from the slurry removed here. The dry materials moves down the kiln.

(b) Calcination zone: It is the middle part of the kiln. The temperature of kiln here is ~ 1000⁰C. All the organic matter present in raw materials burnt here and calcium carbonate decomposes to form CaO and CO₂.



(c) Burning zone or clinkering zone: It is the hottest and lower most portion of the kiln. The temperature here is 1400-1600⁰C. 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.

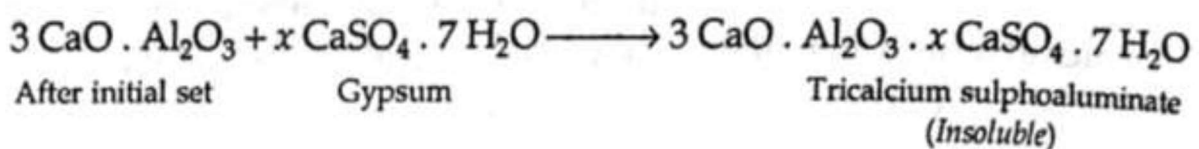
• **Clinkering Zone :**



The calcium aluminates and silicates combine together to form small (of about 0.5 cm to 1 cm diameter), hard, round greyish stone which is known as clinkers. These clinkers are very hot (is about 1000°C.). The rotary kiln at the base is provided with another small rotary kiln. In these hot clinkers fall and cool air is admitted from opposite direction. Air Counter-blast cools the clinkers. Hot air so-produced is used for burning powdered coal. The cooled clinkers are collected in small trolley.

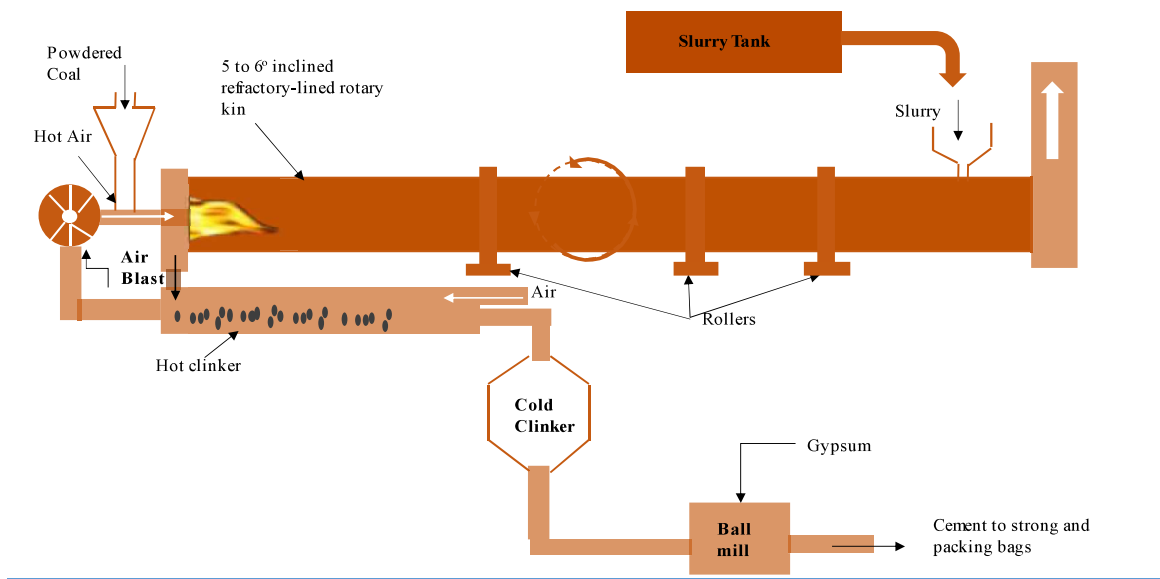
(iii) Cooling zone: The clinkers produced by above procedure are cooled by a stream of air. It is an important process in order to produce a definite degree of crystallization of the melted clinkers.

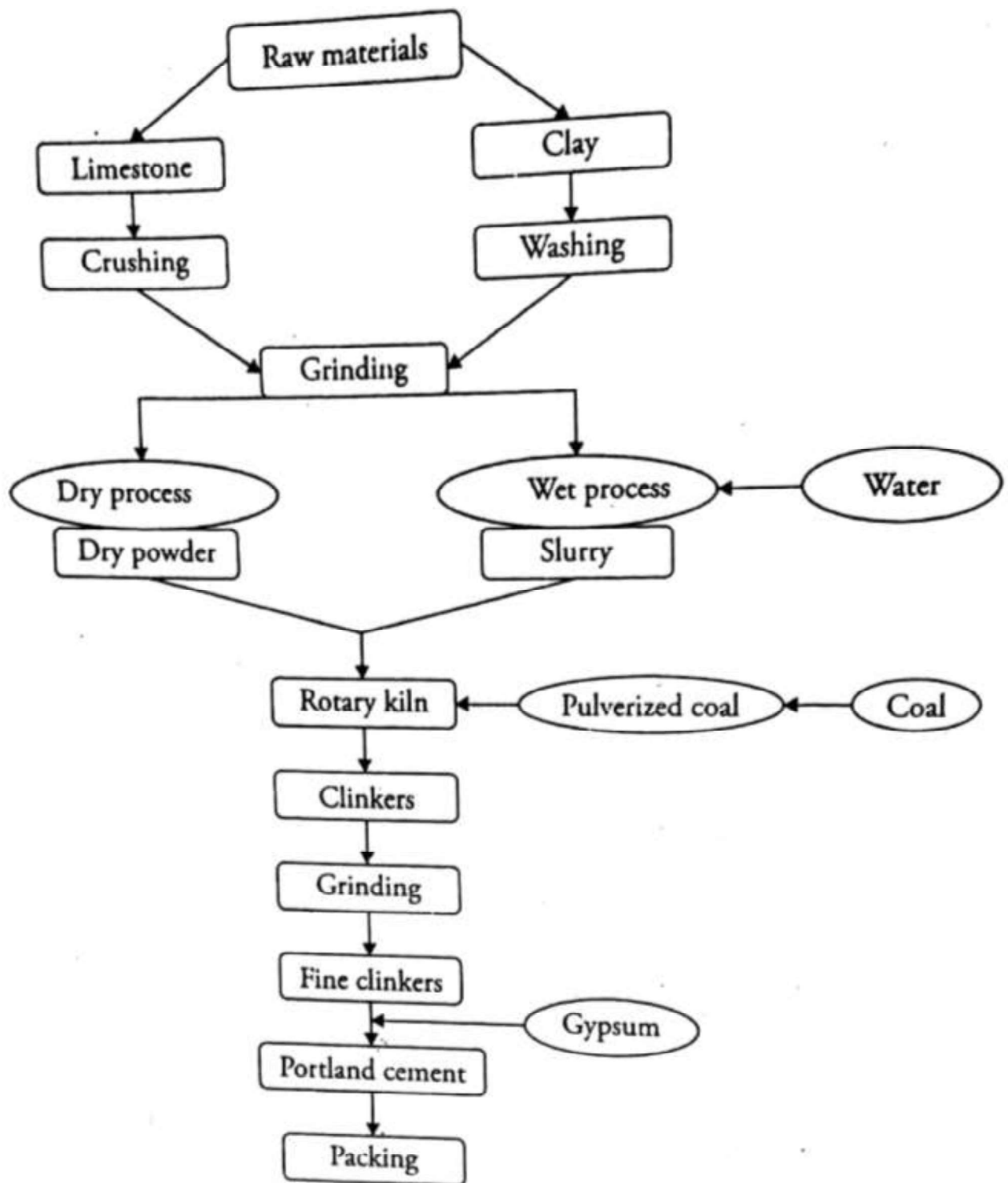
(iv) Grinding: The cooled clinkers are ground in ball mill with the addition of 2-5 % of gypsum. The finely ground clinkers set very quickly when they come in contact with water. Gypsum (CaSO₄.2H₂O) acts as a retarding agent and delays this setting. When cement is mixed with water, the initial sets take place due to hydration of tricalcium aluminate. Gypsum reacts with tricalcium aluminate and forms insoluble tricalcium sulfoaluminate which does not hydrate quickly.



(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.

Fig. Rotary Cement Klin





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

Setting and hardening of cement:

When cement is mixed with water and allowed to stand it 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 material 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, precipitates out as gel or crystals. These insoluble gels surround inert materials like sand and crushing stones and bind them strongly. It is believed 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 believed that the setting times of tricalcium aluminate (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.

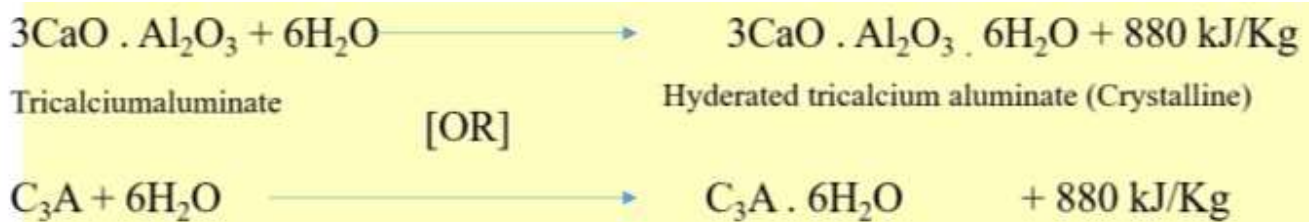


Setting is the stiffening of original plastic mass due to the formation of tobermorite gel". It can be divided into 2 stages a) Initial Set b) Final Set

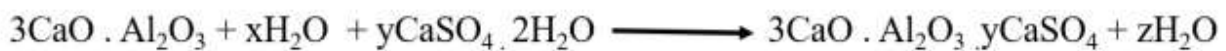
- Initial Set is when paste begins to stiffen
- Final Set is when the paste begins to harden and is able to sustain some loads

Hardening is the development of strength due to formation of crystals"

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 aluminoferrite. The hydration of tricalcium aluminate (C₃A) takes place within a day.

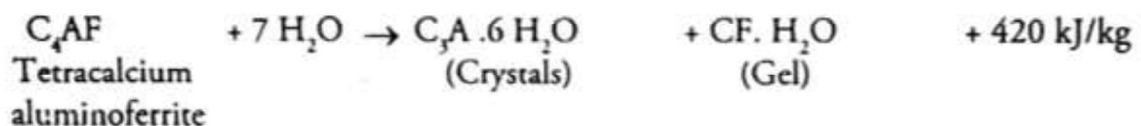
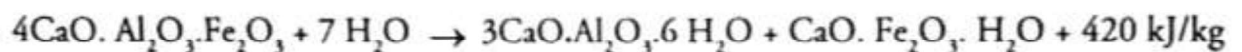


Tricalcium aluminate (C₃A) combines with water very rapidly with the evolution of large amount of heat. Flash set is not desirable as it causes loss of workability of cement and prevents hydration of other constituent of cement. Adding gypsum retards the dissolution of C₃A by forming *insoluble Tricalcium sulpho-aluminate*.



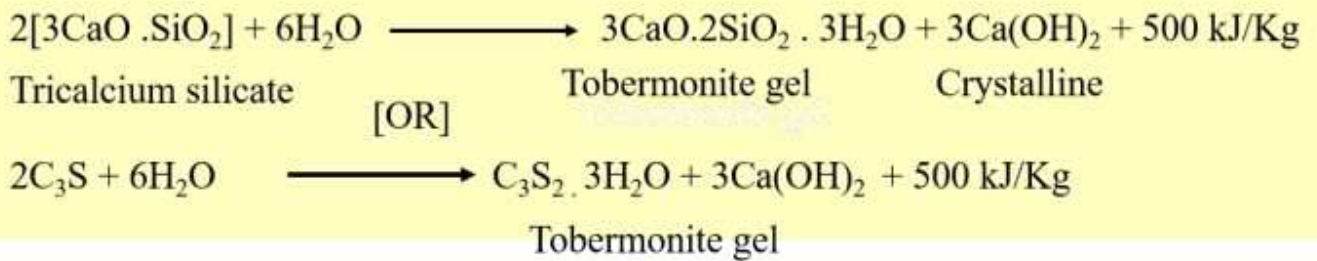
Where $z = 7 - 32 \text{ H}_2\text{O}$

b) Tetracalcium aluminoferrite also undergoes hydrolysis forming crystalline products.



(c) Days 2-7

After hydration of C₃A, C₃S begins to hydrate to give tobermonitegel and crystalline Ca(OH)₂, which is responsible for initial strength of the cement. The hydration of C₃S gets completed within 7 days.

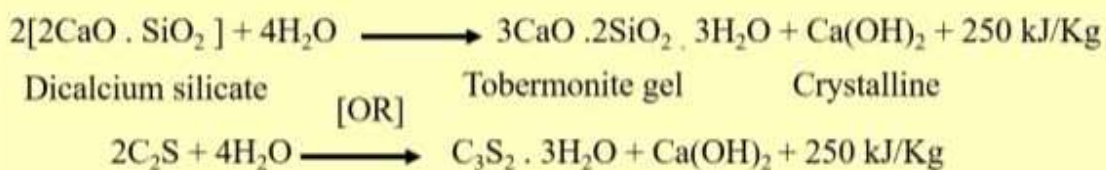


Tobermonite gel possesses a very high surface area and very high adhesive property

(d) Final setting and hardening:

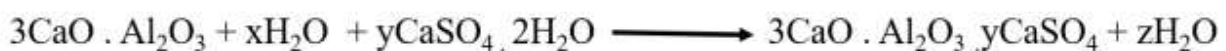
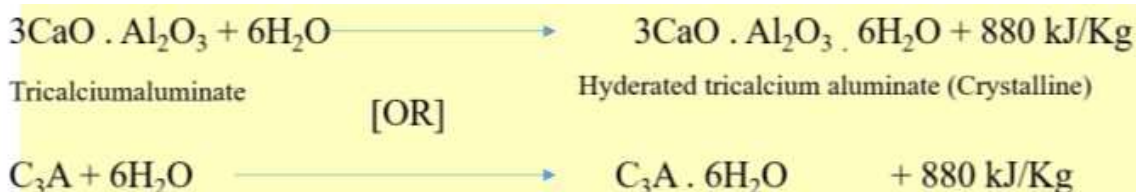
Day – 7 to 28 :

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



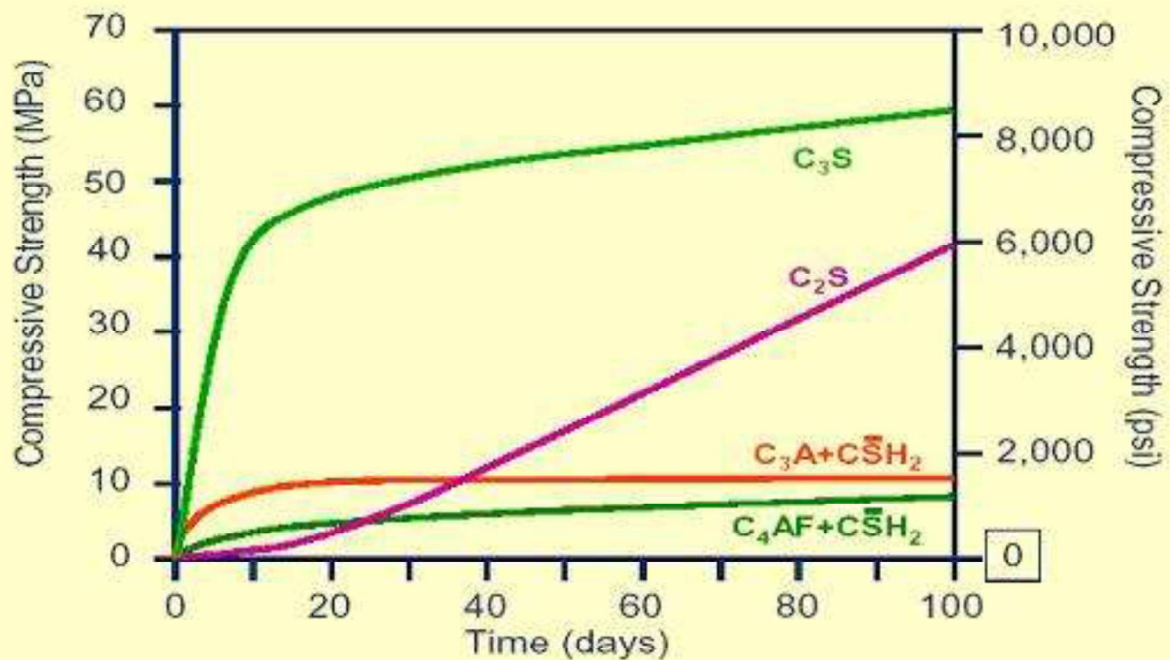
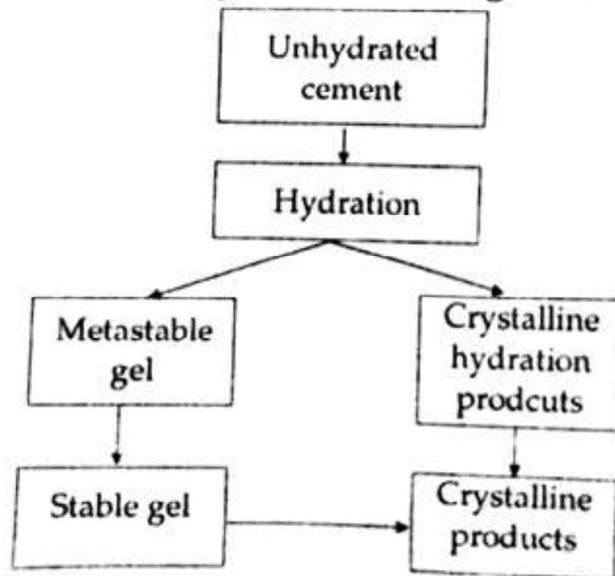
Increase of strength is due to formation of tobermonite gel and crystallizing Ca(OH)_2 of both C_2S and C_3S

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 as 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 sulfo-aluminate*.



Where $z = 7-32 \text{ H}_2\text{O}$

The setting and hardening of cement



CHEMICAL COMPOSITION OF CEMENT

According to I.S. 269 – 1975, composition of ordinary Portland cement shall satisfy the following conditions :

(1) Ratio of the percentage of lime (CaO) to that of silica (SiO₂), alumina (Al₂O₃) and iron oxide (Fe₂O₃), when calculated by the formula :

$$\frac{\text{CaO} - 0.7 \text{ SO}_3}{2.8 \text{ SiO}_2 + 1.2 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3}$$

shall not be less than 0.66 and more than 1.02.

(2) Ratio of percentage of alumina (Al₂O₃) to that of iron oxide (Fe₂O₃) shall *not be less than 0.66*

(3) Weight of *insoluble residue* shall not exceed 2 percent.

(4) Weight of magnesia shall not be more than 6 percent.

(5) Total sulphur contents, calculated as sulphuric anhydride (SO₃), shall not be more than 2.75 percent.

(6) Total loss on ignition shall not exceed 4 percent.

Notes : In the manufacture of Portland cement, great care is taken to see that the composition satisfies the above.

(i) *If too much lime is present, the cement will be 'unsound', that is, after sometime concrete made from it will expand and crack.*

(ii) *If too little lime is present, the concrete will be low in strength and may 'set quickly', i.e., hardens before the mason has a chance to place it in the forms.*

(iii) *Cement in which alumina is high is also apt to be quick-setting and hard to burn uniformly.*

(iv) *High silica cements are, usually, very slow hardening and do not attain their full strength for a considerable period.*

Physical requirements of cement : (1) **Setting time :** Initial : Not less than 30 minutes ; Final : Not more than 600 minutes.

(2) **Compressive strength** (of 1 : 3 cement mortar cube of cement and Ennore sand) :

3 days : Not less than 1.6 kg/mm² (or 16 N/mm²).

7 days : Not less than 2.2 kg/mm² (or 22 N/mm²).

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 $\sim 1500-1600^{\circ}\text{C}$ in rotary kiln and grinding resulting mass in to fine powders.

(i) Composition: 35- 40% CaO ; 35-55% Al_2O_3 ; 5 – 15% $\text{FeO} + \text{Fe}_2\text{O}_3$; 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 $\text{CaAl}(\text{OH})_5 \cdot 3\text{H}_2\text{O}$.

(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 [$3MgO \cdot MgCl_2 \cdot 11H_2O$]. 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 resistance 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 ($\text{Na}_2\text{O} \cdot n\text{SiO}_2$) or potassium silicate ($\text{K}_2\text{O} \cdot n\text{SiO}_2$) 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 be 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