

Cement

Concrete is most widely used non-metallic material in construction of buildings, dams, bridges, high ways etc. In concrete, cement is the essential bonding material which binds sand and rock when mixed with water.

Cement is a binder, a substance that sets and hardens and can bind other materials together. Cements used in construction can be characterized as being either hydraulic or non-hydraulic, depending upon the ability of the cement to be used in the presence of water. Non-hydraulic cement will not set in wet conditions or underwater, rather it sets as it dries and reacts with carbon dioxide in the air. It can be attacked by some aggressive chemicals after setting. Hydraulic cement is made by replacing some of the cement in a mix with activated aluminium silicates, pozzolanas, such as fly ash. The chemical reaction results in hydrates that are not very water-soluble and so are quite durable in water and safe from chemical attack. This allows setting in wet condition or underwater and further protects the hardened material from chemical attack (e.g., Portland cement).

Cement is a dirty greenish heavy powder and finds its importance as a building material. It can be described as material possessing adhesive and cohesive properties and capable of bonding materials like stones, bricks, building blocks etc. Cement has the property of setting and hardening in the presence of water. So it is called as hydraulic cement. The essential constituents of cement used for constructional purposes are compounds of calcium (calcareous) and Al +Si (argillaceous).

Classification: -Cement is classified into four types, based on the chemical composition.

1. Natural cement
2. Puzzolona cement
3. Slag cement
4. Portland cement

Of these, Portland cement is the most widely used cement

Portland cement: It is most widely used non-metallic material of construction. It is a mixture of calcium silicates and calcium aluminates with small amount of gypsum.

The name Portland cement is used because this powder on mixing with water gives a hard, stone like mass which resembles Portland rock.

Properties:-All Portland cements are hydraulic in nature

Composition of Portland cement:- A good sample of Portland cement contains

- Calcium Oxide or lime (CaO) : 60%
- Silica (SiO₂) : 20-24%
- Alumina (Al₂O₃) : 5-7.5%

- Magnesia (MgO) : 2-3%
- Ferric Oxide (Fe₂O₃) : 1-2.5%
- Sulphur trioxide (SO₃) : 1-1.5%
- Sulphur Oxide (Na₂O) : 1%
- Potassium Oxide (K₂O) : 1%

Portland cement Manufacturing

Manufacturing of cement involves various raw materials and processes. Each process is explained chemical reactions for manufacture of Portland Cement.

Cement is a greenish grey colored powder, made of calcined mixtures of clay and limestone. When mixed with water becomes a hard and strong building material.

Mixing of raw material

The major raw materials used in the manufacture of cement are Calcium, Silicon, Iron and Aluminum. These minerals are used in different form as per the availability of the minerals.

Table shows the raw materials for Portland cement manufacture

Calcareous Materials	Argillaceous Materials		
Calcium	Silicon	Aluminum	Iron
Limestone	Clay	Clay	Clay
Marl	Marl	Shale	Iron ore
Calcite	Sand	Fly ash	Mill scale
Aragonite	Shale	Aluminum ore refuse	Shale
Shale	Fly ash		Blast furnace dust
Sea Shells	Rice hull ash		
Cement kiln dust	Slag		

The mixing procedure of the manufacture of cement is done by 2 methods,

Dry process

Wet process

a) Dry Process

The both calcareous and argillaceous raw materials are firstly crushed in the gyratory crushers to get 2-5cm size pieces separately. The crushed materials are again grinded to get fine particles into ball or tube mill.

Each finely grinded material is stored in hopper after screening. Now these powdered minerals are mixed in required proportion to get dry raw mix which is then stored in silos and kept ready to be sent into rotary kiln. Now the raw materials are mixed in specific proportions so that the average composition of the final product is maintained properly.

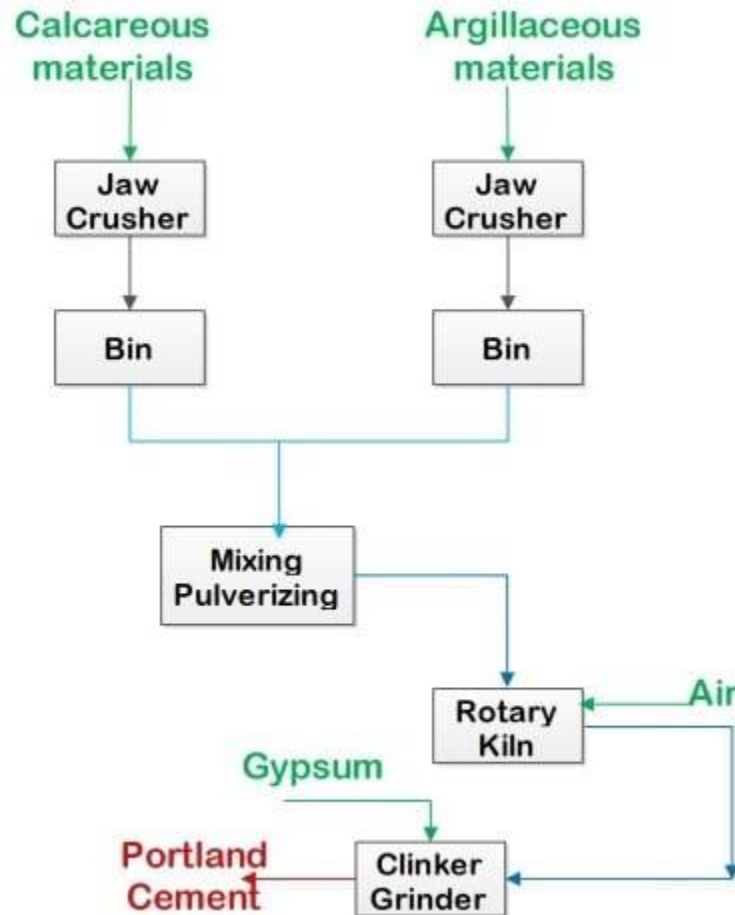


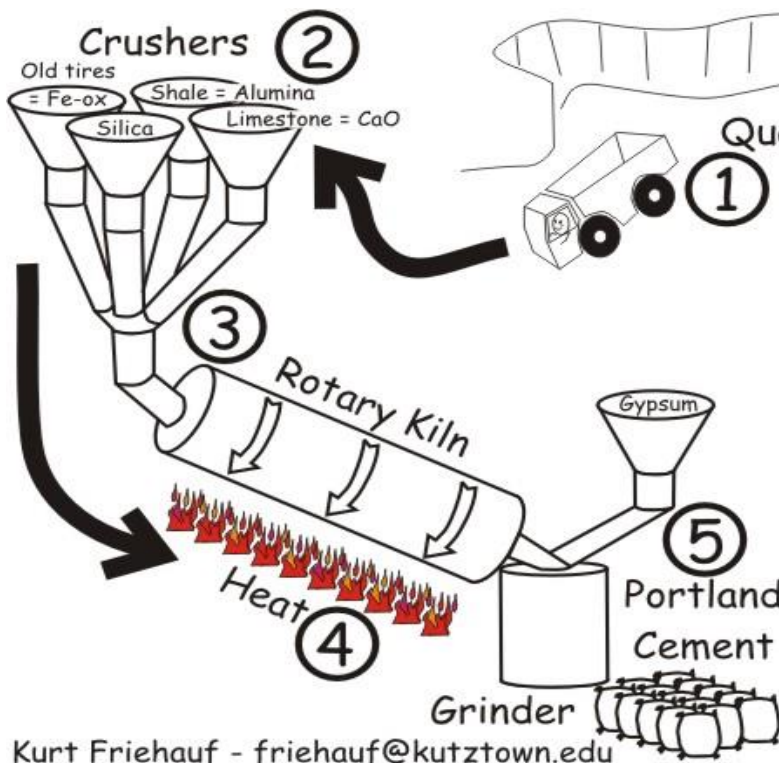
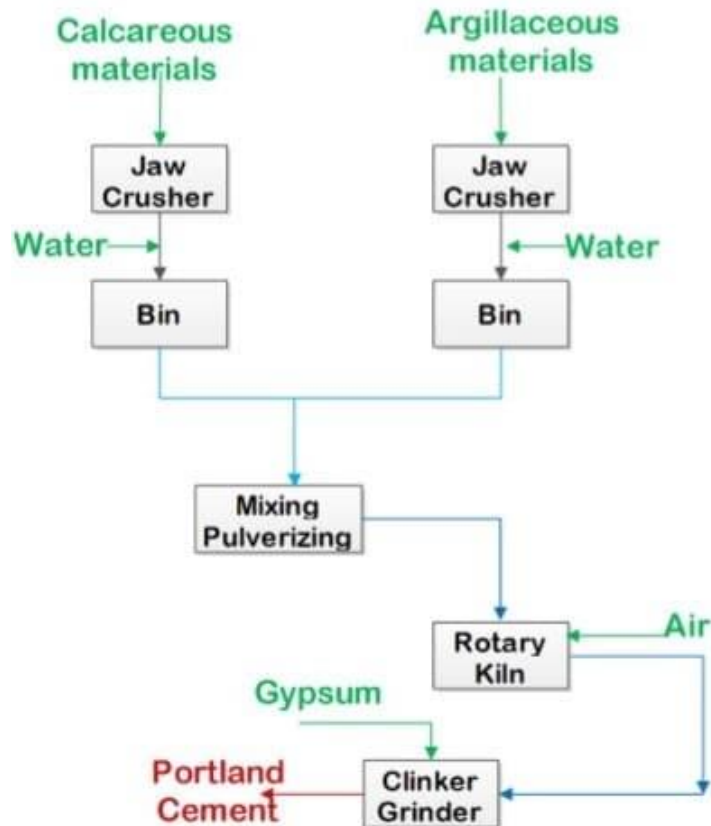
Fig: Manufacture of Cement by Dry Process

b) Wet Process

The raw materials are firstly crushed and made into powdered form and stored in silos. The clay is then washed in washing mills to remove adhering organic matters found in clay.

The powdered limestone and water washed clay are sent to flow in the channels and transfer to grinding mills where they are completely mixed and the paste is formed, i.e., known as slurry.

The grinding process can be done in ball or tube mill or even both. Then the slurry is led into collecting basin where composition can be adjusted. The slurry contains around 38-40% water that is stored in storage tanks and kept ready for the rotary kiln.



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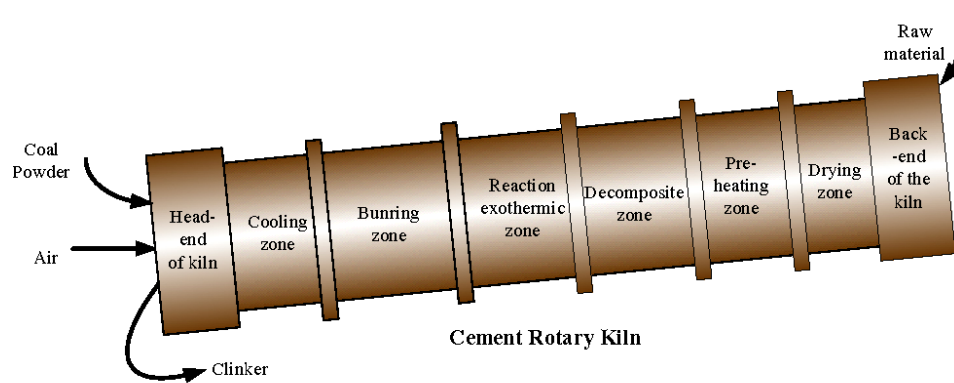


TABLE 10.1
ZONES IN ROTARY CEMENT KILNS

	Temperature range of material	
	°C	°F
Drying and preheating zone	15-805	60-1480
Calcining zone	805-1200	1480-2192
Upper-transition zone	1200-1400	2192-2552
Sintering zone	1400-1510	2552-2750
Cooling (lower-transition) zone	1510-1290	2750-2350

Comparison of dry process and wet process of Cement Manufacture

Criteria	Dry process	Wet process
Hardness of raw material	Quite hard	Any type of raw material
Fuel consumption	Low	High
Time of process	Lesser	Higher
Quality	Inferior quality	Superior quality
Cost of production	High	Low
Overall cost	Costly	Cheaper
Physical state	Raw mix (solid)	Slurry (liquid)

2. Burning of Raw Materials

The burning process is carried out in the rotary kiln while the raw materials are rotated at 1-2rpm at its longitudinal axis. The rotary kiln is made up of steel tubes having the diameter of 2.5-3.0 meter and the length differs from 90-120meter. The inner side of the kiln is lined with refractory bricks.

The kiln is supported on the columns of masonry or concrete and rested on roller bearing in slightly inclined position at the gradient of 1 in 25 to 1 in 30. The raw mix of dry process of corrected slurry of wet process is injected into the kiln from the upper end. The kiln is heated with the help of powdered coal or oil or hot gases from the lower end of the kiln so that the long hot flames is produced.

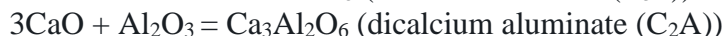
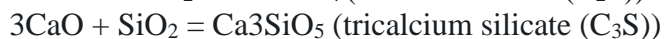
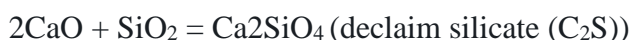
As the kiln position is inclined and it rotates slowly, the material charged from upper end moves towards lower end at the speed of 15m/hr. In the upper part, water or moisture in the material is evaporated at 400oC temp, so this process is known as Drying Zone.

The central part i.e. calcination zone, the temperature is around 10000C, where decomposition of lime stone takes place. The remaining material is in the form of small lumps known as nodules after the CO₂ is released.



The lower part (clinkering zone) have temperature in between 1500-17000C where lime and clay are reacts to yielding calcium aluminates and calcium silicates. This aluminates and silicates of calcium fuse to gather to form small and hard stones are known as clinkers. The size of the clinker is varies from 5-10mm.

The lower part i.e. clinkering zone has the temperature around 1500-1700C. In the region lime and clay reacts to yield calcium aluminates and calcium silicates. This products of aluminates and silicates of calcium fuses together to form hard and small stones known as clinkers. The size of the small and hard clinkers varies from 5 to 10mm.

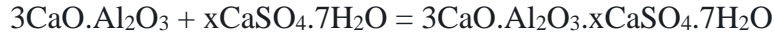


The clinker coming from the burning zone are very hot. To bring down the temperature of clinkers, air is admitted in counter current direction at the base of the rotary kiln. The cooled clinkers are collected in small trolleys.

3. Grinding of Clinkers

The cooled clinkers are received from the cooling pans and sent into mills. The clinkers are grinded finely into powder in ball mill or tube mill. Powdered gypsum is added around 2-3% as retarding agent during final grinding. The final obtained product is cement that does not settle quickly when comes in contact with water.

After the initial setting time of the cement, the cement becomes stiff and the gypsum retards the dissolution of tri-calcium aluminates by forming tricalcium sulfoaluminate which is insoluble and prevents too early further reactions of setting and hardening.



4. Storage and packaging

The grinded cement is stored in silos, from which it is marketed either in container load or 50kg bags.

Chemical compounds of Portland cement

The proportions of the chemical compounds of cement vary in the various Portland cements. Table represents the composition and percentage of found compounds for Portland cement.

Compound	Formula	Shorthand form	% by weight	Properties of cement compounds
Alite or tricalcium silicate	Ca_3SiO_4	C3S	50 - 70%	<ul style="list-style-type: none"> <input type="checkbox"/> It is responsible for early strength <input type="checkbox"/> First 7 days strength is due to C3S <input type="checkbox"/> It produces more heat of hydration <input type="checkbox"/> Cement with more C3S is better for cold weather concreting.
Belite or dicalcium silicate	Ca_2SiO_5	C2S	15 - 30%	<ul style="list-style-type: none"> <input type="checkbox"/> <input type="checkbox"/> C2S hydrates after 7 days. Hence, it gives strength after 7 days. <input type="checkbox"/> <input type="checkbox"/> C2S hydrates and harden slowly and provides much of the ultimate strength <input type="checkbox"/> <input type="checkbox"/> It produces less heat of hydration. <input type="checkbox"/> <input type="checkbox"/> Responsible for long term strength
Tricalcium aluminate	$\text{Ca}_3\text{Al}_2\text{O}_6$	C3A	5 - 10%	<ul style="list-style-type: none"> <input type="checkbox"/> The reaction of C3A with water is very fast and may lead to an immediate stiffening of paste, and this process is termed as flash set. <input type="checkbox"/> To prevent this flash set, 2 to 3% gypsum is added at the time of grinding the cement clinkers. <input type="checkbox"/> C3A liberates a lot of heat during the early stages of hydration, but has little (almost none) strength contribution. <input type="checkbox"/> Cement low in C3A is sulfate resistant.
Tetracalcium aluminoferrite	$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$	C4AF	5-15%	<ul style="list-style-type: none"> <input type="checkbox"/> It hydrates very rapidly. <input type="checkbox"/> Contributes very little strength of concrete even though

				<input type="checkbox"/> Also responsible for grey colour of Ordinary Portland Cement <input type="checkbox"/> The hydrates of C4AF show a comparatively higher resistance to sulphate attack than the hydrates of C3A
Sodium oxide	Na ₂ O	N	0.5 - 1.3%	
Potassium oxide	K ₂ O	K		
Gypsum	CaSO ₄ .2H ₂ O	CSH ₂		

Composition of Cement clinker

The various constituents combine in burning and form cement clinker. The compounds formed in the burning process have the properties of setting and hardening in the presence of water. They are known as Bogue compounds after the name of Bogue who identified them. These compounds are as follows: Alite (Tricalcium silicate or C3S), Belite (Dicalcium silicate or C2S), Celite (Tricalcium aluminate or C3A) and Felite (Tetracalcium aluminoferrite or C4AF).

Tricalcium silicate

It is supposed to be the best cementing material and is well burnt cement. It is about 25-50% (normally about 40 per cent) of cement. It renders the clinker easier to grind, increases resistance to freezing and thawing, hydrates rapidly generating high heat and develops an early hardness and strength. However, raising of C3S content beyond the specified limits increases the heat of hydration and solubility of cement in water. The hydrolysis of C3S is mainly responsible for 7 day strength and hardness. The rate of hydrolysis of C3S and the character of gel developed are the main causes of the hardness and early strength of cement paste. The heat of hydration is 500 J/g.

Dicalcium silicate

It constitutes about 25-40% (normally about 32 per cent) of cement. It hydrates and hardens slowly and takes long time to add to the strength (after a year or more). It imparts resistance to chemical attack. Rising of C2S content renders clinker harder to grind, reduces early strength, decreases resistance to freezing and thawing at early ages and decreases heat of hydration. The hydrolysis of C2S proceeds slowly. At early ages, less than a month, C2S has little influence on strength and hardness. While after one year, its contribution to the strength and hardness is proportionately almost equal to C3S. The heat of hydration is 260 J/g.

Tricalcium aluminate

It is about 5-11% (normally about 10.5 per cent) of cement. It rapidly reacts with water and is responsible for flash set of finely ground clinker. The rapidity of action is regulated by the addition of 2-3% of gypsum at the time of grinding cement. Tricalcium aluminate is responsible for the initial

set, high heat of hydration and has greater tendency to volume changes causing cracking. Raising the C3A content reduces the setting time, weakens resistance to sulphate attack and lowers the ultimate strength, heat of hydration and contraction during air hardening. The heat of hydration of 865 J/g.

Tetracalciumalumino ferrite

It constitutes about 8–14% (normally about 9 per cent) of cement. It is responsible for flash set but generates less heat. It has poorest cementing value. Raising the C4AF content reduces the strength slightly. The heat of hydration is 420 J/g.

Hydration of Cement

In the anhydrous state, four main types of minerals are normally present: alite, belite, celite and felite. Also present are small amounts of clinker sulfate (sulfates of sodium, potassium and calcium) and gypsum, which was added when the clinker was ground up to produce the familiar grey powder.

When water is added, the reactions which occur are mostly exothermic, that is, the reactions generate heat. We can get an indication of the rate at which the minerals are reacting by monitoring the rate at which heat is evolved using a technique called conduction calorimetry. Almost immediately on adding water some of the clinker sulphates and gypsum dissolve producing an alkaline, sulfate-rich, solution. Soon after mixing, the (C3A) phase (the most reactive of the four main clinker minerals) reacts with the water to form an aluminate rich gel (Stage I on the heat evolution curve above). The gel reacts with sulfate in solution to form small rod-like crystals of ettringite. (C3A) reaction with water is strongly exothermic but does not last long, typically only a few minutes, and is followed by a period of a few hours of relatively low heat evolution. This is called the dormant, or induction period (Stage II). The first part of the dormant period, up to perhaps half-way through, corresponds to when concrete can be placed. As the dormant period progresses, the paste becomes too stiff to be workable. At the end of the dormant period, the alite and belite in the cement start to react, with the formation of calcium silicate hydrate and calcium hydroxide. This corresponds to the main period of hydration (Stage III), during which time concrete strengths increase. The individual grains react from the surface inwards, and the anhydrous particles become smaller. (C3A) hydration also continues, as fresh crystals become accessible to water. The period of maximum heat evolution occurs typically between about 10 and 20 hours after mixing and then gradually tails off. In a mix containing OPC only, most of the strength gain has occurred within about a month. Where OPC has been partly-replaced by other materials, such as fly ash, strength growth may occur more slowly and continue for several months or even a year. Ferrite reaction also starts quickly as water is added, but then slows down, probably because a layer of iron hydroxide gel forms, coating the ferrite and acting as a barrier, preventing further reaction.

Products of Hydration

During Hydration process several hydrated compounds are formed most important of which are, Calcium silicate hydrate, calcium hydroxide and calcium aluminium hydrates which is important for strength gain.

Calcium silicate hydrate:

This is not only the most abundant reaction product, occupying about 50% of the paste volume, but it is also responsible for most of the engineering properties of cement paste. It is often abbreviated, using cement chemists' notation, to "C-S-H," the dashes indicating that no strict ratio of SiO_2 to CaO is inferred. C-S-H forms a continuous layer that binds together the original cement particles into a cohesive whole which results in its strong bonding capacity. The Si/Ca ratio is somewhat variable but typically approximately 0.45-0.50 in hydrated Portland cement but up to perhaps about 0.6 if slag or fly ash or micro silica is present, depending on the proportions.

Calcium hydroxide:

The other products of hydration of C_3S and C_2S are calcium hydroxide. In contrast to the CS-H, the calcium hydroxide is a compound with distinctive hexagonal prism morphology. It constitutes 20 to 25 per cent of the volume of solids in the hydrated paste. The lack of durability of concrete is on account of the presence of calcium hydroxide. The calcium hydroxide also reacts with sulphates present in soils or water to form calcium sulphate which further reacts with C_3A and cause deterioration of concrete. This is known as sulphate attack. To reduce the quantity of $\text{Ca}(\text{OH})_2$ in concrete and to overcome its bad effects by converting it into cementitious product is an advancement in concrete technology. The use of blending materials such as fly ash, silica fume and such other pozzolanic materials are the steps to overcome bad effect of $\text{Ca}(\text{OH})_2$ in concrete. However, $\text{Ca}(\text{OH})_2$ is alkaline in nature due to which it resists corrosion in steel.

Calcium aluminium hydrates:

These are formed due to hydration of C_3A compounds. The hydrated aluminates do not contribute anything to the strength of concrete. On the other hand, their presence is harmful to the durability of concrete particularly where the concrete is likely to be attacked by sulphates. As it hydrates very fast it may contribute a little to the early strength

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

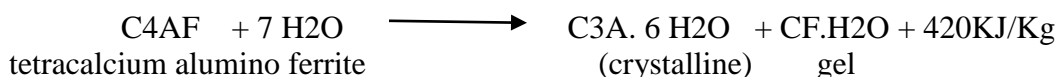
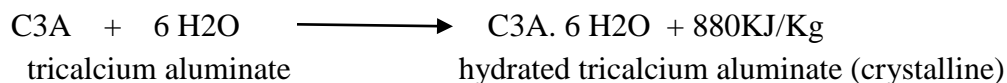
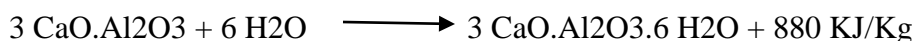
(ii) hardening

Setting is defined as stiffening of the original plastic mass due to initial gel formation. Hardening is development of strength, due to crystallisation.

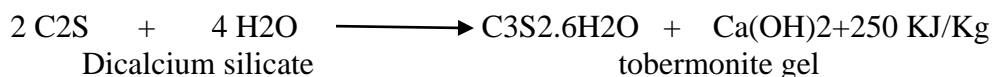
Due to the gradual progress of crystallisation in the interior mass of cement, hardening starts after setting. The strength developed by cement paste at any time depends upon the amount of gel formed and the extent of crystallisation. The setting and hardening of cement is due to the formation of inter locking crystals reinforced by rigid gels formed by the hydration and hydrolysis of the constitutional compounds.

Reactions involved in setting and hardening of cement:-

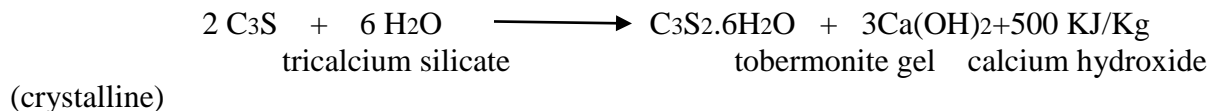
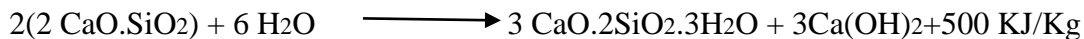
When cement is mixed with water, the paste becomes rigid within a short time which is known as initial setting. This is due to the hydration of tricalcium aluminate and gel formation of tetra calcium aluminato ferrite.



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



Final setting and hardening of cement paste is due to the formation of tobermonite gel and crystallisation of calcium hydroxide and hydrated tricalcium aluminate.



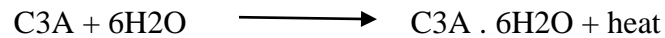
During setting and hardening of cement, some amount of heat is liberated due to hydration and hydrolysis reactions. The quantity of heat evolved during Complete hydration of cement is 500 KJ/Kg.

Sequence of chemical reactions during setting & hardening:-

Cement *1 day* *hydration of* *7 days* *gelation* *28 days* *gelation*
 + -----> *C3A and* -----> *of* -----> *of*
Water paste *C4AF* *C3S* *C2S & C3S*

Function of gypsum in cement:-

Tri calcium aluminate (C3A) combines with water very rapidly.



After the initial setting, the paste becomes soft and the added gypsum retards the dissolution of C3A by forming insoluble calcium sulpho aluminate. $3 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x \text{CaSO}_4 \cdot 7 \text{H}_2\text{O}$

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