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MATERIALS CHEMISTRY

CEMENT

In the most general sense of the word, a cement is a binder, a substance that sets and hardens independently, and can bind other materials together. Cement is construction material which possess adhesive and cohesive properties and used for binding the building blocks, bricks, stones. The cements of interest in the making of concrete have the property of setting and hardening under water by virtue of a chemical reaction with it and are, therefore, called hydraulic cement. The name "Portland cement" given originally due to the resemblance of the color and quality of the hardened cement to Portland stone – Portland island in England.

History of the origin of cement:

John Smeaton made an important contribution to the development of cements when he was planning the construction of the third Eddystone Lighthouse (1755) in the English Channel. He needed a hydraulic mortar that would set and develop some strength in the twelve hour period between successive high tides.

In 1824, Joseph Aspdin patented a similar material, which he called Portland cement, because the render made from it was in colour similar to the prestigious Portland stone.

The investigations of L.J. Vicat led him to prepare an artificial hydraulic lime by calcining an intimate mixture of limestone and clay.

Later in 1845 Isaac Charles Johnson burnt a mixture of clay and chalk till the clinkering stage to make better cement and established factories in 1851. The German standard specification for Portland cement was drawn in 1877.

The British standard specification was first drawn up in 1904. The first ASTM specification was issued in 1904.

In India, Portland cement was first manufactured in 1904 near Madras, by the South India Industrial Ltd. But this venture failed.

Between 1912 and 1913, the Indian Cement Co. Ltd., was established at Porbander (Gujarat) and by 1914 this Company was able to deliver about 1000 tons of Portland cement.

Classification:

Cement is classified into 4 types based on chemical composition.

(1)Natural cement: It is made by subjecting the argillaceous lime stone to calcinations at high temperature and then the calcinated mass is pulverized. If possesses low strength and used in preparation of mortors.

(2)Puzzalona cement: Natural puzzalona is deposit of volcanic ash which is produced by rapid cooling of lava mixed with slaked lime. It is a mixture of aluminium silicate, calcium silicate and silicates of iron. Puzzalona cement is not used directly but used by mixing with Portland cement.

(3)Slag cement: Slag cement is mixture of slag i.e. aluminium silicate and calcium. The mixture is poured into cold water, granular cement produced is dried and mixed with lime and pulverized to fine powder. Slag cement is low setting cement. It can be hardened by adding accelerators like clay, salt or caustic soda. It is used for making concrete for construction in waterlogged area where much tensile strength is not required.

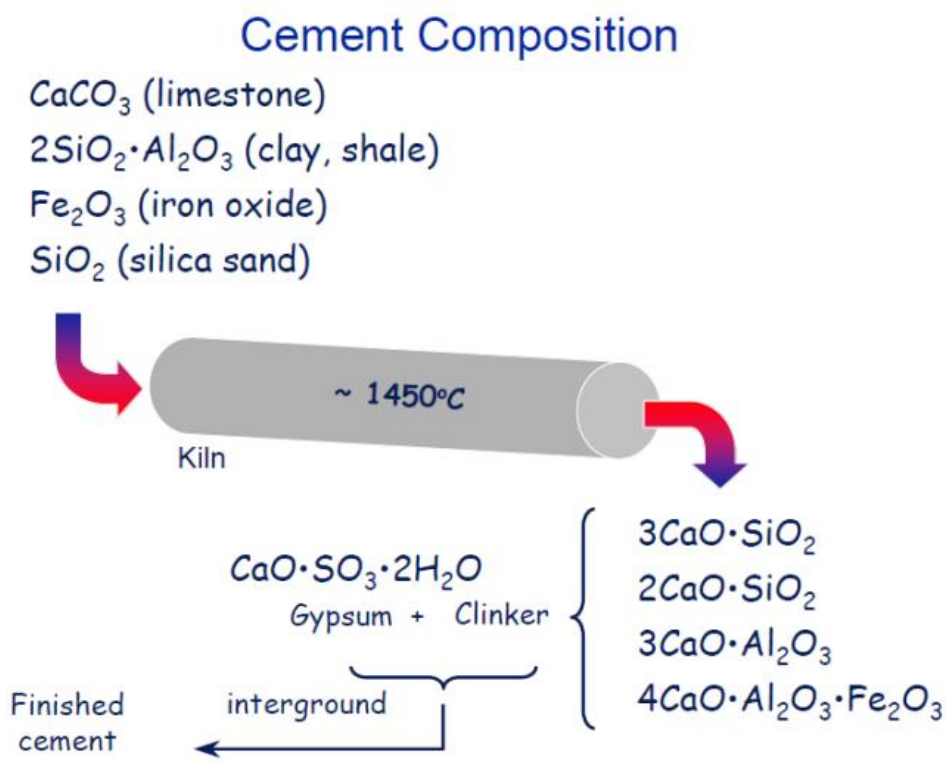
(4)Portland cement: Portland cement is made by calcination of calculated amounts of clay and lime followed by gypsum. It is a mixture of calcium silicate and aluminium silicate with small amount of gypsum. It is hydraulic in nature.

Chemical composition of Portland cement:

The raw materials used for the manufacture of cement consist mainly of lime, silica, alumina and iron oxide. These oxides interact with one another in the kiln at high temperature to form more complex compounds. The relative proportions of these oxide compositions are responsible for influencing the various properties of cement; in addition to rate of cooling and fineness of grinding.

Table: Chemical composition range of Portland cement

Ingradient	Formula	% limit	Functions
Lime	CaO	60-67	Increases strength and setting time
Silica	SiO_2	17-25	Gives strength and prolongs setting time
Alumina	Al_2O_3	3-8	Increases strength
Iron oxide	Fe_2O_3	0.5-6.0	Imparts grey color and strength
Magnesia	MgO	0.1-4.0	Excess % contributes to unsoundness
Sulfur trioxide	SO_3	1.2	Imparts soundness
Alkali	$Na_2O + K_2O$	0.5-3.0	Causes efflorescence



Manufacture of Portland cement:

There are two different methods for the manufacture of Portland cement:

(1)*Dry process*: Grinding and mixing of the raw materials in their dry state.

(2)*Wet process*: Grinding and mixing of the raw materials in the existence of water.

(i) Manufacture of cement by Dry process:

The quarried clay and limestone are crushed separately until nothing bigger than a tennis ball remains. Samples of both rocks are then sent off to the laboratory for mineral analysis.

The dry process involves different steps: The process is used when raw materials lime stone and clay is hard.

(a) Mixing of raw materials

(b)Burning mixture in rotary kiln

(c) Grinding clinkers with gypsum.

(a) Mixing of raw materials: The dry process produces fine powder of cement. This process is employed if limestone and clay are hard. The lime stone is crushed into pieces and it is mixed with clay in 3:1 ratio. The mixture is pulverized to fine powder and stored in storage bins and then introduced into upper end of rotary kiln for calcinations.

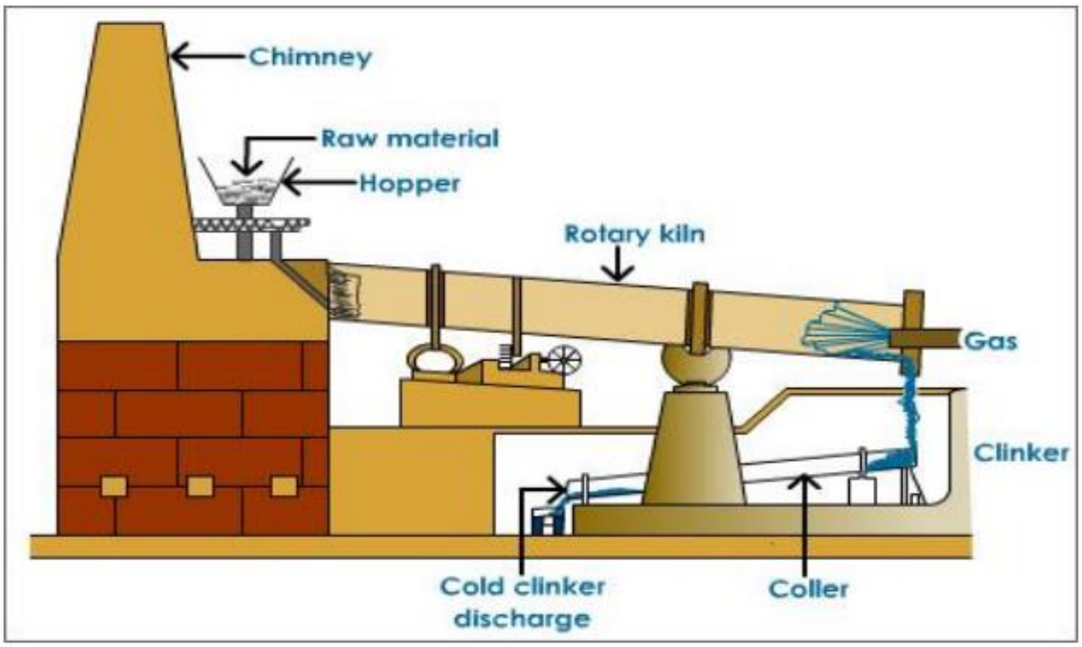


Fig: Manufacture of cement by Dry process

(b)Burning of mixture in rotary kiln: The rotary kiln consists of an inclined steel cylinder 15-200 ft long and 10 ft diameter. It is mounted on rollers and can be rotated with desired speed. The cylinder is lined inside with fire bricks. The kiln has different zones.

(i) The drying zone: The zone is present in upper part of kiln and temperature is around 400^0C. Here water present in the slurry gets evaporated and clay is cleaved to Al_2O_3, SiO_2 and Fe_2O_3

$$Al_2O_3.SiO_2.Fe_2O_3.2H_2O \rightarrow Al_2O_3 + SiO_2 + Fe_2O_3 + 2H_2O$$

(ii)Calcination zone or decarbonating zone: This is middle portion of kiln, where the temperature is 10000 C. Here the lime stone is completely decomposed into CaO which exists in the form of small lumps called nodules.

$$CaCO_3 \rightarrow CaO + CO_2$$

(iii) Burning zone or clinkering zone: This is bottom most and hottest zone in rotary kiln. The temperature is around 1400^0C-1500^0C. In this zone the mixture melts and forms little rounded pasty mass called clinkers. The clinkers are greenish black and have rough texture. In the burning zone or clinkering zone the following reactions take place.

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

Dicalcium silicate

$$3CaO + SiO2 \rightarrow 3CaO.SiO_2\ (C_3S)$$

Tricalcium silicate

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

Tricalcium aluminate

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

(tetracalcium aluminoferrite)

The C_3A + C_4AF/C_3S ratio is known as burn ability index. This is generally in the range 0.45-0.85.

(C) Grinding or mixing of cement clinkers with gypsum: The clinkers are cooled and finely ground. The finely ground clinkers have low setting time and by absorption of moisture they set quickly. To reduce rate of setting it is mixed with 2-3% gypsum ($CaSO_4.2H_2O$). The fast setting Al_2O_3 in clinkers reacts with gypsum and form crystals of tricalcium sulfo aluminate which is insoluble. This prevents early setting and hardening. The mixture of clinkers and gypsum is known as Portland cement.

(ii) Manufacture of cement by wet process:

The clay is mixed to a paste in a washmill - a tank in which the clay is pulverised in the presence of water. Crushed lime is then added and the whole mixture further ground. This method is used when both the raw materials lime stone and clay is hard. The manufacture of cement by wet process involves three different steps.

(1)Mixing of raw materials: The organic matter and foreign materials present in the clay are removed by washing with water. The lime stone is mixed with clay in 3:1 proportion and then homogenized. The resulting slurry contains 40% water. The slurry is fed into rotary kiln.

(2)Calcinations or burning of mixture in rotary kiln: The slurry of raw mixture is fed into rotary kiln. The kiln consists of an inclined rotating cylinder 150-200 ft long and 10 ft in diameter, lined with fire bricks. The kiln rotates at the rate of one revolution per minute. Due to rotary motion of kiln the slurry moves downwards and gets heated, by blast of hot air. The chemical reactions taking place at various zones of rotary kiln are-

(a) Drying zone: The temperature in the zone is 750^0C, the moisture present in the slurry is evaporated and the clay is broken into Al_2O_3, SiO_2 and Fe_2O_3.

$$Al_2O_3 .2SiO_2. Fe_2O_3. 2H_2O \rightarrow Al_2O_3 + SiO_2 + Fe_2O_3 + 2H_2O$$

(Clay)

(b)Calcinations zone: The temperature in this zone is 10000 C and lime stone gets decomposed to CaO

$$CaCO_3 \rightarrow CaO + CO_2$$

(c)*Reaction zone or clinkering zone:* The temperature in this zone is about 1600^0 C, the mixture partly gets melted and following chemical reactions takes place.

$$2CaO + SiO_2 \rightarrow 2CaO.SiO_2$$

$$3CaO + SiO_2 \rightarrow 3CaO.SiO_2$$

The resulting product called clinker, is allowed to cool in cooler.

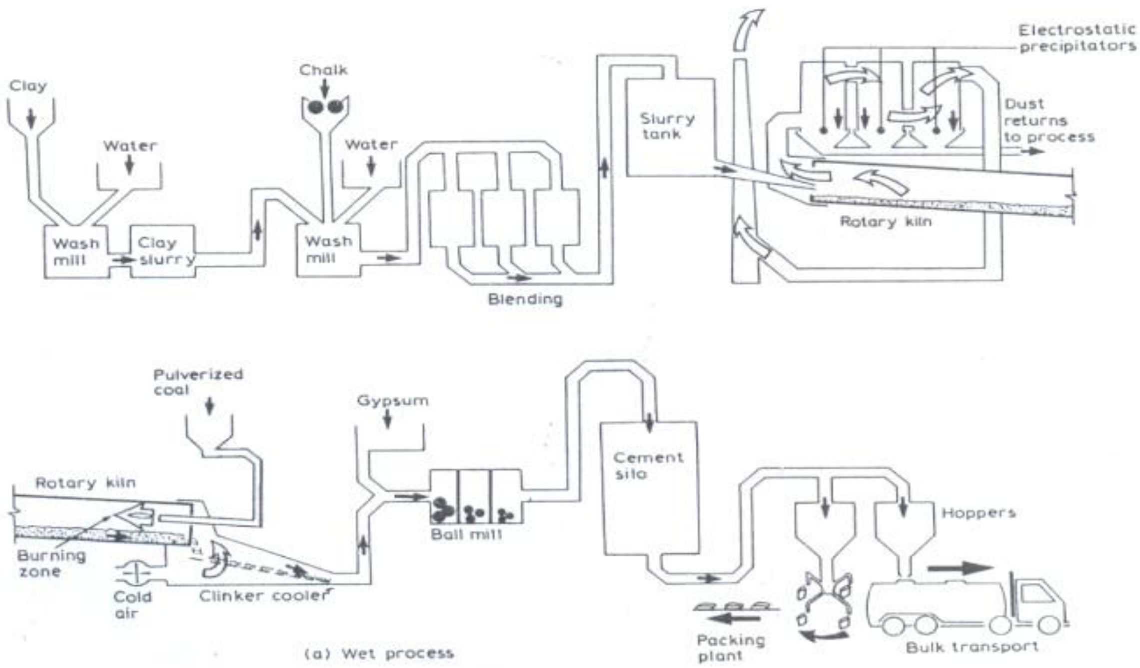


Fig: Manufacture of cement by Wet process

(3)Mixing of clinkers of cement with gypsum: The clinkers are mixed with 3% gypsum to reduce the rate of setting. The fast setting constituent Al_2O_3 of clinker reacts with gypsum to form calcium sulpho aluminate.

The cement manufacturing process consist of the following multi stages as explain in the following flow chart.

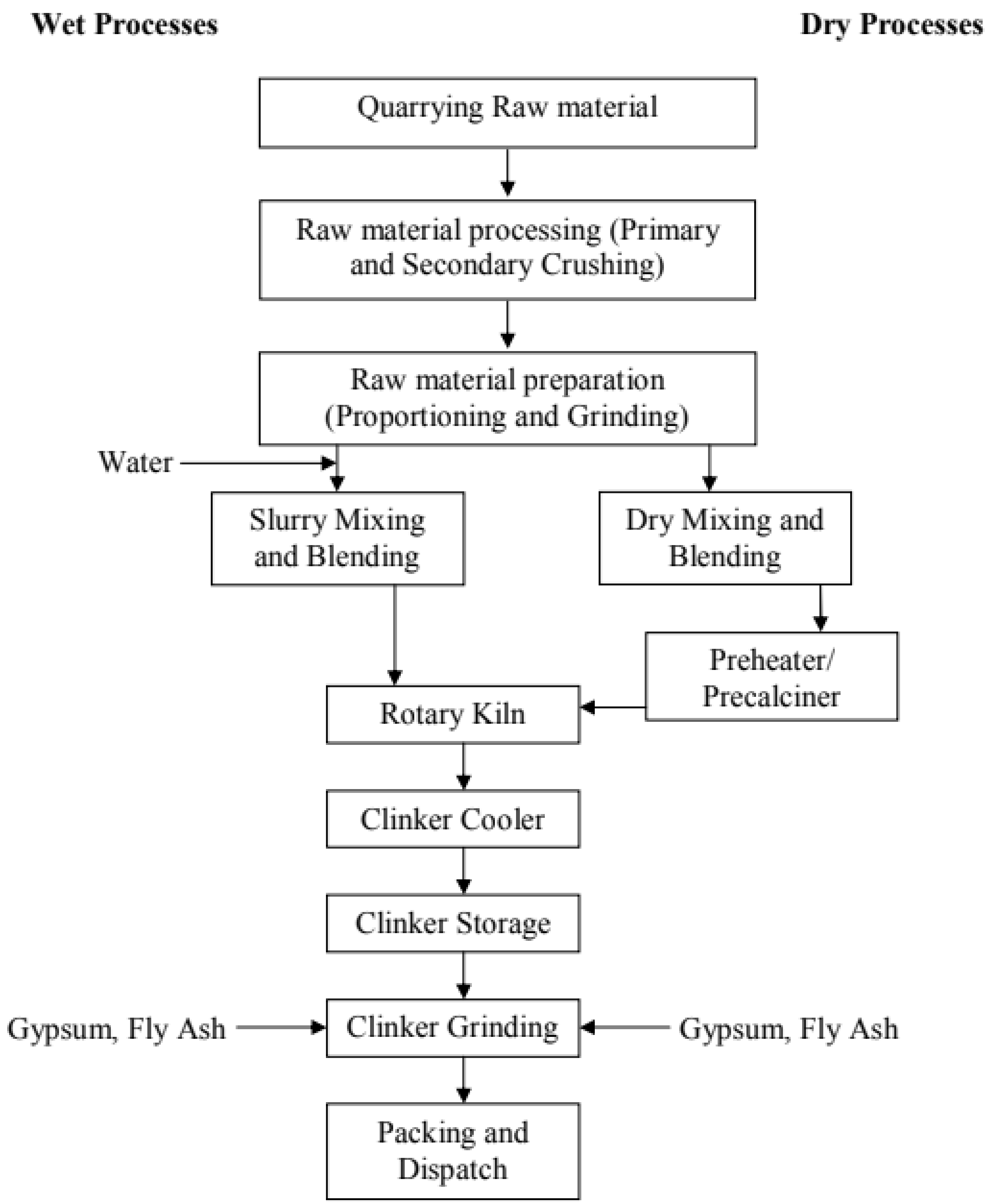


Fig: Flow Diagram of Cement Manufacturing Process

Comparison between wet and dry process

S.N	Wet process	Dry process
1	Moisture content of the slurry is 35-50%	Moisture content of the pellets is 12%
2	Size of the kiln needed to manufacture the cement is bigger	Size of the kiln needed to manufacture the cement is smaller
3	The amount of heat required is higher, so the required fuel amount is higher	The amount of heat required is lower, so the required fuel amount is lower
4	Less economically	More economically
5	The raw materials can be mix easily, so a better homogeneous material can be obtained	Difficult to control the mixing of raw materials process, so it is difficult to obtain homogeneous material
6	The machinery and equipments do not need much maintenance	The machinery and equipments need more maintenance

Hydration of cement:

When Portland cement is mixed with water its chemical compound constituents undergo a series of chemical reactions that cause it to harden. This chemical reaction with water is called "hydration".

Each one of these reactions occurs at a different time and rate. Together, the results of these reactions determine how Portland cement hardens and gains strength. Hydration starts as soon as the cement and water are mixed. The rate of hydration and the heat liberated by the reaction of each compound is different.

Each compound produces different products when it hydrates.

Tricalcium silicate (C_3S): Hydrates and hardens rapidly and is largely responsible for initial set and early strength. Portland cements with higher percentages of C_3S will exhibit higher early strength.

Tricalcium aluminate (C_3A): Hydrates and hardens the quickest. Liberates a large amount of heat almost immediately and contributes somewhat to early strength. Gypsum is added to Portland cement to retard C_3A hydration. Without gypsum, C_3A hydration would cause Portland cement to set almost immediately after adding water.

Dicalcium silicate (C_2S): Hydrates and hardens slowly and is largely responsible for strength increases beyond one week.

Tetracalcium aluminoferrite (C_4AF): Hydrates rapidly but contributes very little to strength. Its use allows lower kiln temperatures in Portland cement manufacturing. Most Portland cement color effects are due to C_4AF.

- **Reactions of Hydration**
  - $2C_3S + 6H = C_3S_2H_3 + 3Ca(OH)_2$

    $(100 + 24 = 75 + 49)$
  - $2\,C_2S + 4H = C_3S_2H_3 + Ca(OH)_2$

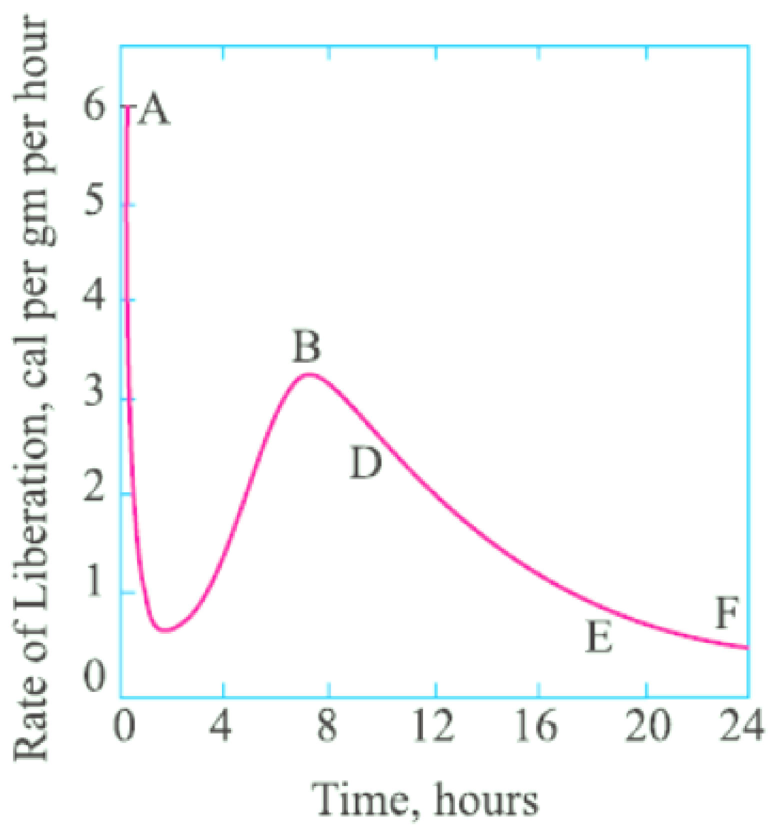
    $(100 + 21 = 99 + 22)$
  - $C_3A + 6H = C_3AH_6$

    $[C_3A + CaSO_4 . 2H_2O = 3CaO. Al_2O_3. 3CaSO_4. 31H_2O]$

    Calcium Sulfoaluminate

The reaction of cement with water is exothermic. The reaction liberates a considerable quantity of heat. This liberation of heat is called heat of hydration. This is clearly seen if freshly mixed cement is put in a vacuum flask and the temperature of the mass is read at intervals. The study and control of the heat of hydration becomes important in the construction of concrete dams and other mass concrete constructions. It has been observed that the temperature in the interior of large mass concrete is 50°C above the original temperature of the concrete mass at the time of placing and this high temperature is found to persist for a prolonged period.

The heat of hydration is the heat generated when water and Portland cement react. Heat of hydration is most influenced by the proportion of C3S and C3A in the cement, but is also influenced by water-cement ratio, fineness and curing temperature. As each one of these factors is increased, heat of hydration increases. For usual range of Portland cements, about one-half of the total heat is liberated between 1 and 3 days, about three-quarters in 7 days, and nearly 90 percent in 6 months. The heat of hydration depends on the chemical composition of cement.



Properties of Hydrated Cement Compounds

1	Tricalcium silicate (alite)	C_3S	• Hydrates & hardens rapidly • Responsible for initial set and early strength
2	Dicalcium silicate (belite)	C_2S	• Hydrates & hardens slowly • Contributes to later age strength (beyond 7 days)
3	Tricalcium aluminate	C_3A	• Liberates a large amount of heat during first few days • Contributes slightly to early strength development • Cements with low % ages are more resistant to sulphates
4	Tetracalcium alumino ferrite (ferrite)	C_4AF	• Reduces clinkering temperature • Hydrates rapidly but contributes little to strength • Colour of hydrated cement (gray) due to ferrite hydrates

Heat of hydration of cement:

The quantity of evolved heat when the cement hydrated completely at a given temperature – Joule/gram or calorie/gram of unhydrated cement. The hydration of cement compounds - accompanied with heat evolution, energy of up to 120 cal/g of cement being liberated.

The heat of hydration, as measured, consists of the chemical heat of the reactions of hydration and the heat of adsorption of water on the surface of the gel formed by the processes of hydration. The latter heat accounts for about a quarter of the total heat of hydration. Thus, the heat of hydration is really a composite quantity

The Factors affecting of heat of hydration :

1- The chemical composition of the cement Heat of hydration of cement = sum of the heats of hydration of the individual compounds when hydrated separately. The contribution of individual compounds to the total heat of hydration of cement can be measured from the following equation:

Heat of hydration of 1 g of cement

$$= 136(C_3S) + 62(C_2S) + 200(C_3A) + 30(C_4AF)$$

2- Ambient temperature – has great effect on the rate of heat evolution – The rate of heat evolution increase with increase in the ambient temperature.

3- Type of cement: Types of cement can be arranged in descending order with respect to their rate of heat evolution, as follows: -

(i) Rapid hardening Portland cement.

(ii) Ordinary Portland cement.

(iii) Modified Portland cement.

(iv)Sulfate resistant Portland cement.

(v) Low heat Portland cement.

4- Fineness of cement: An increase in fineness speed up the reactions of hydration and therefore the heat evolved. It is reasonable to assume that the early rate of hydration of each compound in cement is proportional to the surface area of the cement. However, at later ages, the effect of the surface area is negligible and the total amount of heat evolved is not affected by the fineness of cement.

5- Amount of cement in the mixture: The quantity of cement in the mix also affects the total heat development: thus the richness of the mix, that is, the cement content, can be varied in order to help the control of heat development.

Setting of cement:

Setting of cement is a complicated process. It is important to distinguish setting from hardening, which refers to the gain of strength of a set cement paste. On addition of water, the calcium compound re decomposed with the formation of free $Ca(OH)_2$ and hydrate crystalline silicate and calcium aluminate, the crystal of which form an interlaced mass. Due to this interlacing of crystals the setting of cement occurs. The following equation represent these reactions:

$$C_2S + xH_2O \rightarrow C_2S.xH_2O \text{ (amorphous)}$$

$$C_3S + xH_2O \rightarrow C_2S\ .\ (x-1)H_2O \text{ (amorphous)} + Ca(OH)_2$$

$$C_3A + 6H_2O \rightarrow C_3A.6H_2O$$

The hydration products have very low solubility of water.

Cement + water → cement paste → lose its plasticity gradually→ when it lose its plasticity completely → setting occurs.

The two first to react are C3A and C3S. The setting time of cement decreases with a rise in temperature. The importance of setting in concrete works comes from the importance to keep the fresh concrete in the plastic stage for enough time necessary to complete its mixing and placing under practical conditions. But, from the economical side, it is important that the concrete hardens at convenient period after casting.

Flash setting – Occurs when there is no gypsum added or exhausting the gypsum ($CaSO_4.2H_2O$ added with little amount), so C_3A reacts violently with water causing liberation high amount of heat causing rapid setting of cement, and leading to form porous microstructure that the product of hydration of the other compounds precipitate through, unlike the normal (ordinary) setting that have much lower porosity microstructure. The following equations represent these reactions:

$$C_3A + 6H_2O \rightarrow C_3A.6H_2O$$

$$C_3A + 3(CaSO_4.2H_2O) + 25H_2O \rightarrow C_3A\ .\ 3CaSO4\ .\ 31H_2O$$

$$C_4AF + xH_2O \rightarrow C_3A.6H_2O + CaO.Fe_2O_3\ .\ (x\text{-}6)\ H2O$$

$$MgO + H_2O \rightarrow Mg(OH)_2$$

The various compounds contribute to the heat of setting as follows:

$$C_3A > C_3S > C_4AF > C_2S$$

There are four main stages during setting:

Stage I - Takes only few minutes after the addition of water to the cement. The rate of heat generation is high, due to wetting of cement particles with water, and the beginning of hydrolysis and reaction of the cement compounds. After that the rate decreases to relatively low value.

stage II(dormant period) : Takes 1-4 hours with relatively low speed. The initial layer of the hydration begins slowly to build on the cement particles. Bleeding and sedimentation appears at this period.

Stage III: Heat of hydration begins to rise again due to the dissolution of the weak gel layer formed in the beginning (first) on the surface of C3S crystals – so the water able to surround the particles surfaces again – and forming gel of calcium silicates with enough amount to increase setting. The activity reach its peak after about 6 hours for cement paste, with standard consistency, and might be late for paste with higher w/c ratio. At the end of the stage, the paste reaches the final setting stage.

Stage IV: Hardening and gain of strength Vicat apparatus , use to measure the setting time for cement paste. Initial setting time – refers to the beginning of the cement paste setting. Final setting time – refers to the beginning of hardening and gain of strength.

Iraqi Standard Specification No. 5 limits: Initial setting time not less than 45 minutes. Final setting time not more than 10 hours.

Factors affecting the setting :

1. Water/cement (w/c) ratio – The setting time of cement increases with the increase of w/c ratio.

2. Temperature and relative humidity - The setting time of cement decreases with a rise in temperature and decrease of relative humidity.

3. Fineness of cement - The setting time of cement decreases with a rise in fineness of cement.

4- Chemical composition