
Portland Cement

Cement: is a material with adhesive and cohesive properties which make it capable of bonding minerals fragments into a compact whole.

For constructional purposes, the meaning of the term "cement" is restricted to the bonding materials used with stones, sand, bricks, building stones, etc.

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.

Manufacture of Portland cement:

Raw materials

- Calcareous material – such as limestone or chalk, as a source of lime (CaO).
- Clayey material – such as clay or shale (soft clayey stones), as a source of silica and alumina.

Methods of cement manufacturing:

- 1- Wet process:** grinding and mixing of the raw materials in the existence of water.
- 2- Dry process:** grinding and mixing of the raw materials in their dry state.

The process to be chosen, depend on the nature of the used raw materials.

- ✓ **Wet process:** the percentage of the moisture in the raw materials is high.
- ✓ **Dry process:**
 - The raw materials is so hard (solid) that they do not disintegrate by water
 - Cold countries, because the water might freeze in the mixture
 - Shortage of the water needed for mixing process.

Wet process:

When chalk is used, it is finely broken up and dispersed in water in a wash mill. The clay is also broken up and mixed with water, usually in a similar washmill. The two mixtures are now pumped so as to mix in predetermined proportions and pass through a series of screens. The resulting – cement slurry – flows into storage tanks.

When limestone is used, it has to be blasted, then crushed, usually in two progressively smaller crushers (initial and secondary crushers), and then fed into a ball mill with the clay dispersed in water. The resultant slurry is pumped into storage tanks. From here onwards, the process is the same regardless of the original nature of the raw materials.

The slurry is a liquid of creamy consistency, with water content of between 35 and 50%, and only a small fraction of material – about 2% - larger than a 90 μm (sieve No. 170).

The slurry mix mechanically in the storage tanks, and the sedimentation of the suspended solids being prevented by bubbling by compressed air pumped from bottom of the tanks.

The slurry is analyzed chemically to check the achievement of the required chemical composition, and if necessary, the mix constituents are changed to attain the required chemical composition.

Finally, the slurry with the desired lime content passes into the **rotary kiln**. This is a large, refractory-lined steel cylinder, up to 8 m in diameter, sometimes as long as 230 m, which is slightly inclined to the horizontal.

The slurry is fed in at the upper end while pulverized coal (oil or natural gas also might be used as a fuel) is blown in by an air blast at the lower end of the kiln, where the temperature reaches about 1450°C.

The slurry, in its movement down the kiln, encounters a progressively higher temperature. At first, the water is driven off and CO₂ is liberated; further on, the dry material undergoes a series of chemical reactions until finally, in the hottest part of the kiln, some 20 to 30% of the material becomes liquid, and lime, silica and alumina recombine. The mass then fuses into balls, 3 to 25 mm in diameter, **known as clinker**. The clinker drops into coolers.

Dry process:

The raw materials are crushed and fed in the correct proportions into a grinding mill, where they are dried and reduced in size to a fine powder. The dry powder, **called raw meal**, is then pumped to a blending silo, and final adjustment is now made in the proportions of the materials required for the manufacture of cement. To obtain a uniform mixture, the raw meal is blended in the silo, usually by means of compressed air.

The blended meal is sieved and fed into a rotating dish called a **granulator**, water weighing about 12% of the meal being added at the same time. In this manner, hard pellets about 15 mm in diameter are formed.

The pellets are baked hard in a pre-heating grate by means of hot gases from the kiln. The pellets then enter the kiln, and subsequence operations are the same as in the wet process of manufacture.

Comparison between wet and dry process:

Wet process	Dry process
1- Moisture content of the slurry is 35-50%	1- Moisture content of the pellets is 12%
2- Size of the kiln needed to manufacture the cement is bigger	2- 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	3- The amount of heat required is lower, so the required fuel amount is lower
4- Less economically	4- More economically
5- The raw materials can be mix easily, so a better homogeneous material can be obtained	5- 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	6- The machinery and equipments need more maintenance

Grinding of the clinker:

The cool clinker (produced by wet or dry process), which is characteristically black and hard, is **interground with gypsum** $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in order to prevent **flash setting** of the cement, and to facilitate the grinding process. The grinding is done in a ball mill. The cement discharged by the mill is passed through a separator, fine particles being removed to the storage silo by an air current, while the coarser particles are passed through the mill once again.

Chemical composition of Portland cement:

The raw materials used in the manufacture of Portland cement consist mainly of lime, silica, alumina and iron oxide. These compounds interact with one another in the kiln to form a series of more complex products and, apart from a small residue of uncombined lime which has not had sufficient time to react, a state of chemical equilibrium is reached. The resultant of firing is the clinker.

Four compounds are usually regarded as the major constituents of cement:

- Tricalcium silicate $3\text{CaO} \cdot \text{SiO}_2$ – (C_3S)
- Dicalcium silicate $2\text{CaO} \cdot \text{SiO}_2$ – (C_2S)
- Tricalcium aluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ – (C_3A)
- Tetracalcium aluminoferrite $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ – (C_4AF)

Where each oxide symbol with one letter:

CaO – C

SiO₂ – S

Al₂O₃ – A

Fe₂O₃ – F

H₂O – H

The rate of cooling affect the degree of crystallization and the amount of amorphous material present in the cooled clinker. The properties of this amorphous material, known as glass, differ considerably from those of crystalline compounds of a nominally similar chemical composition.

The percentage of the main composition of cement can be calculated according to the Bogue equations, based on the assumption that the reactions reached the chemical equilibrium state:

$$C_3S = 4.07 (CaO) - 7.6 (SiO_2) - 6.72 (Al_2O_3) - 1.43 (Fe_2O_3) - 2.85 (SO_3)$$

$$C_2S = 2.87(SiO_2) - 0.754 (C_3S)$$

$$C_3A = 2.65 (Al_2O_3) - 1.69 (Fe_2O_3)$$

$$C_4AF = 3.04 (Fe_2O_3)$$

Where, the terms in brackets represent the percentage of the given oxide in the total mass of cement.

Recently, these compositions are determined by x-ray diffraction.

On cooling below 1250°C, **C₃S** decomposes slowly **but**, if cooling is not too slow, C₃S remains unchanged and is relatively stable at ordinary temperatures.

C₃S which is normally present in the largest amount, occurs as small equidimensional grains.

C₂S is known to have three forms: α - **C₂S**, which exists at high temperatures, inverts to the β -form at about 1450 ° C. β -**C₂S** undergoes further inversion to γ - **C₂S** at about 670°C but, at the rates of cooling of commercial cements, β -**C₂S** is preserved in the clinker.

Usually, silicates in the cement are not pure. It contains secondary oxides which affect the atomic arrangement, the crystal form and properties of the cement during the hydration process.

C₃A forms rectangular crystals, but **C₃A** in frozen glass forms an amorphous interstitial phase.

C₄AF is solid solution ranging from **C₂F** to **C₆A₂F**, but the description **C₄AF** is a convenient simplification.

Minor compounds:

In addition to the main compounds mentioned above, there exist minor compounds, such as **MgO**, **TiO₂**, **Mn₂O₃**, **K₂O** and **Na₂O**. Two of the minor compounds are of particular interest: **K₂O** and **Na₂O**, known as the **alkalis** (about 0.4-1.3% by weight of cement). They have been found to react with the reactive silica found in some aggregates, the products of the reaction causing increase in volume leading to disintegration of the concrete. The increase in the alkalis percentage has been observed to affect the setting time and the rate of the gain of strength of cement.

SO₃: form low percentage of cement weight. **SO₃** comes from the gypsum added (2-6% by weight) during grinding of the clinker, and from the impurities in the raw materials, also from the fuel used through firing process.

Iraqi specification no. 5 limited max. SO_3 by 2.5% when $\text{C}_3\text{A} \leq 7\%$, and by 3% when $\text{C}_3\text{A} > 7\%$.

MgO, present in the cement by 1-4%, which comes from the magnesia compounds present in the raw materials. Iraqi specification no. 5 limited max. MgO by 5%, to control the expansion resulted from the hydration of this compound in the hardened concrete. When the magnesia is in amorphous form, it has no harmful effect on the concrete.

Other minor compounds such as TiO_2 , Mn_2O_3 , P_2O_5 represent $< 1\%$, and they have little importance.

Usual Composition Limits of Portland Cement

Oxide	Content, %
CaO	60-67
SiO_2	17-25
Al_2O_3	3-8
Fe_2O_3	0.5-6
MgO	0.5-4
Alkalis (as Na_2O)	0.3-1.2
SO_3	2.0-3.5

Typical compound composition in ordinary Portland cement

Compound	Content, %
C_3S	54
C_2S	17
C_3A	11
C_4AF	9

Loss on Ignition (L.O.I): It is the loss of the cement sample weight when it expose to the **red temperature (at 1000°C)**. It shows the extent of carbonation and hydration of free lime and free magnesia due to the exposure of cement to the atmosphere. Also, part of the loss in weight comes from losing water from the gypsum composition. The maximum loss on ignition permitted by Iraqi specification no. 5 is 4% by weight.

Insoluble residue: It is that part of cement sample that is insoluble in HCl. It comes from the unreached silica, to form soluble cement compounds diluting in this acid, largely arising from impurities in gypsum. The maximum insoluble residue permitted by Iraqi specification no. 5 is 1.5% by weight.

Bogue's Compounds:

The major Bogue's compounds formed are listed in the table (1). There are also some minor compounds formed but these compounds are not very significant. Two of the minor oxides namely (K_2O) and (Na_2O) referred to as alkalis in cement are important.

The compounds responsible for strength are (Tri calcium silicate (C_3S)) and (Di calcium silicate (C_2S)). They constitute (70 to 80 %) of cement. The average (C_3S) content in modern cement is about (45%) and that of (C_2S) is about 25 %. The sum of the contents of (C_3A) and (C_4AF) has decreased slightly in modern cements.

The equations suggested by Bogue for calculating the percentages of major compounds are given below.

$$C_3S = 4.07 (CaO) - 7.60 (SiO_2) - 6.72 (Al_2O_3) - 1.43 (Fe_2O_3) - 2.85 (SO_3)$$

$$C_2S = 2.87 (SiO_2) - 0.754 (3CaO.SiO_2)$$

$$C_3A = 2.65 (Al_2O_3) - 1.69 (Fe_2O_3)$$

$$C_4AF = 3.04 (Fe_2O_3)$$

Table (1): List of Bogue's Compounds and its Formulae.

Compound	Formula	Short formula
Tri calcium silicate	3 CaO.SiO ₂ C ₃ S	C ₃ S
Di calcium silicate	2 CaO.SiO ₂ C ₂ S	C ₂ S
Tri calcium aluminate	3 CaO.Al ₂ O ₃	C ₃ A
Tetra calcium aluminoferrite	4 CaO.Al ₂ O ₃ .Fe ₂ O ₃	C ₄ AF

The calculated quantity of the compounds in cement varies greatly even for a relatively small change in the oxide composition of the raw materials.

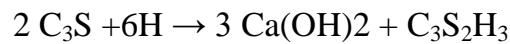
To manufacture a cement of stipulated compound composition, it becomes absolutely necessary to control the oxide composition of the raw materials. For example increasing the lime content will result in unsoundness in cement, and increasing silica content will result in the difficulty to form a clinker. Contents which high total alumina and high ferric oxide will produce cement with high strength.

Hydration of cement:

It is the reaction (series of chemical reactions) of cement with water to form the binding material. In other words, in the presence of water, the silicates (C₃S and C₂S) and aluminates (C₃A and C₄AF) form products of hydration which in time produce a firm and hard mass – **the hydrated cement paste**.

There are two ways in which compounds of the type present in cement can react with water. In the **first**, a direct addition of some molecules of

water takes place, this being a **true reaction of hydration**. The **second type** of reaction with water is **hydrolysis**, in which its nature can be illustrated using the C3S hydration equation:



The rates of the chemical reactions of the main compounds are different:

Aluminates - React with the water in the beginning

- Affect the route of the chemical reactions at early periods of hydration.

Silicates – Affect the later stage reactions.

The hydration of Portland cement involves the reaction of the anhydrous calcium silicate and aluminate phases with water to form hydrated phases. These solid hydrates occupy more space than the anhydrous particles and the result is a rigid interlocking mass whose porosity is a function of the ratio of water to cement (w/c) in the original mix. Provided the mix has sufficient plasticity to be fully compacted, the lower the (w/c), the higher will be the compressive strength of the hydrated cement paste/mortar/concrete and the higher the resistance to penetration by potentially deleterious substances from the environment. Cement hydration is complex and it is appropriate to consider the reactions of the silicate phases (C_3S and C_2S) and the aluminate phases (C_3A and C_4AF) separately.

Cement Hydration Products:

The hydration of Portland cement is rather more complex than that of the individual constituent minerals described above. A simplified illustration of the development of hydrate structure in cement paste is given in Figure (1). When cement is first mixed with water some of the

added calcium sulfate (particularly if dehydrated forms are present and most of the alkali sulfates present dissolve rapidly. If calcium langbeinite is present then it will provide both calcium and sulfate ions in solution, which are available for ettringite formation.

The supply of soluble calcium sulfate controls the (C_3A) hydration, thus preventing a flash set. Ground clinker mixed with water without added calcium sulfate sets rapidly with heat evolution as a result of the uncontrolled hydration of (C_3A). The cement then enters a dormant period when the rate of loss of workability is relatively slow. It will be more rapid; however, at high ambient temperatures (above 25°C).

Setting time is a function of clinker mineralogy (particularly free lime level), clinker chemistry and fineness. The finer the cement and the higher the free lime level, the shorter the setting time in general. Cement paste setting time is arbitrarily defined as the time when a pat of cement paste offers a certain resistance to penetration by a probe of standard cross-section and weight. Setting is largely due to the hydration of (C_3S) and it represents the development of hydrate structure, which eventually results in compressive strength.

The (C–S–H gel) which forms around the larger (C_3S) and (C_2S) grains is formed in situ and has a rather dense and featureless appearance when viewed using an electron microscope.

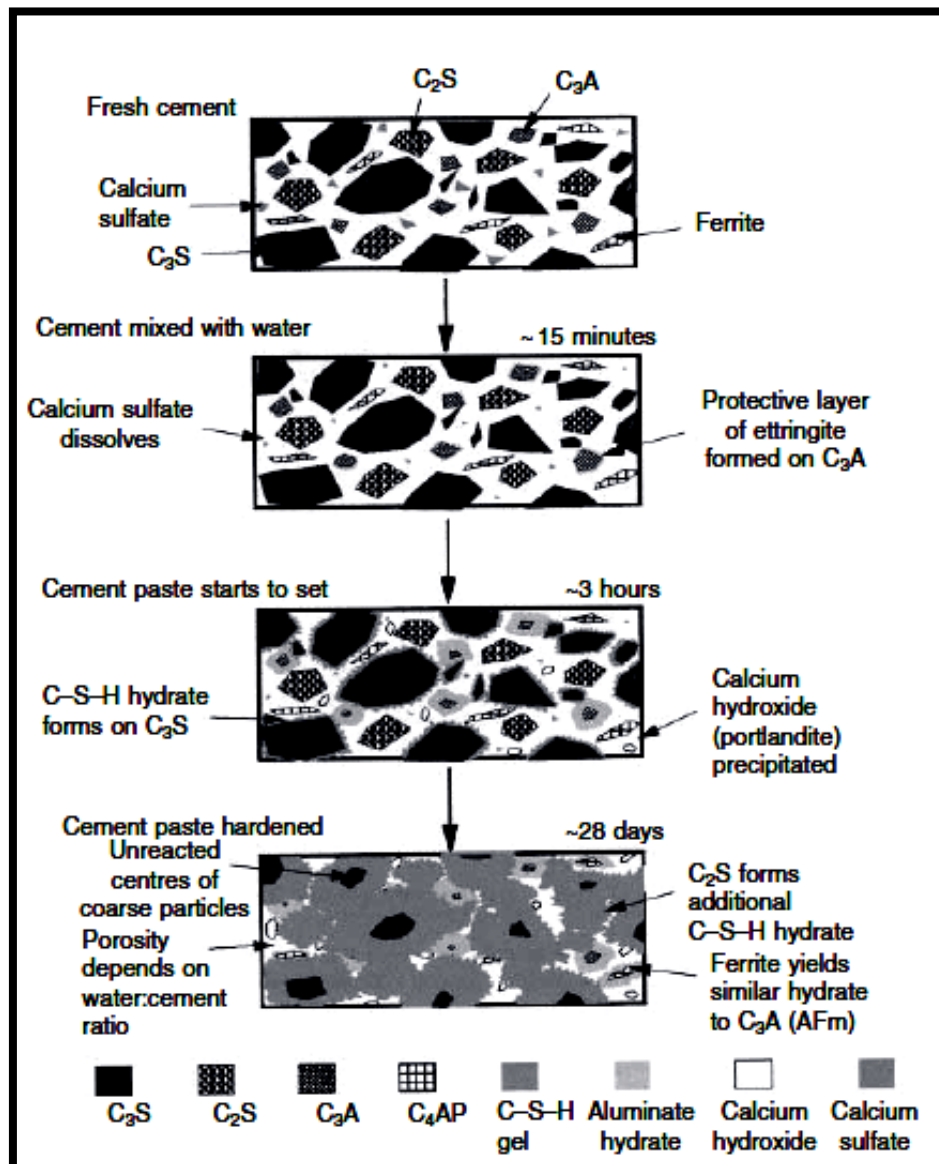
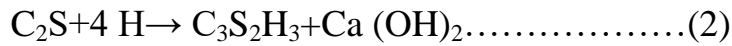


Figure (1): Simplified Illustration of Hydration of Cement Paste.

Calcium Silicate Hydrate (C-S-H):

When (C_3S) and (C_2S) reacts with water, it forms calcium silicate hydrate (C-S-H) and calcium hydroxide ($Ca(OH)_2$), referred hereafter as (CH). (C-S-H) is the most important product of cement hydration, because it is the glue in cementitious materials. Around (50-60%) of cement volume is (C-S-H).

The following equations approximately summarized the hydration reactions:



The reactions are summarized in Table (2). (C_3S) is much more reactive than (C_2S) and under 'standard' temperature conditions of ($20^\circ C$) approximately half of the (C_3S) present in typical cement will be hydrated by (3 days) and (80% by 28) days. In contrast, the hydration of (C_2S) does not normally proceed to a significant extent until ~14 days.

Table (2): The Hydration of Calcium Silicates.

Mineral	Reaction rate	Products of reaction
C_3S	Moderate	C–S–H with Ca:Si ratio ~ 1.7 CH (calcium hydroxide).
C_2S	Slow	C–S–H with Ca:Si ratio ~ 1.7 Small quantity of CH.

Calcium Hydroxide (CH):

The other product of hydration of (C_3S) and (C_2S) is calcium hydroxide ($Ca(OH)_2$) or CH. It is not desirable product in the cementitious materials. Around (50-60%) of cement volume is Calcium Hydroxide.

Calcium Hydroxide will decrease the durability of concrete. (CH) also reacts with sulfate 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.

The use of blending materials such as fly ash, silica fume and other pozzolanic materials is the step to mitigate the problems related to (CH) in concrete. The only advantage (CH), is maintain (pH) value around (13) in the concrete which resists the corrosion of reinforcements.

Calcium Aluminates Hydrates:

The cubic compound (C_3AH_6) is probably the only stable compound formed during the hydration of calcium aluminate which remains stable up to about (225°C). The reaction of pure (C_3A) with water is very fast and may lead to flash set. To prevent this flash set, gypsum is added at the time of grinding the cement clinker. The quantity of gypsum added has a bearing on the quantity of (C_3A) present. The hydrated aluminates do not contribute anything to the strength of concrete. Instead, their presence is harmful to the durability of concrete particularly where the concrete is likely to be attacked by sulfates. As it hydrates very fast it may contribute a little to the early strength upon hydration. (C_4AF) is also believed to form a compound of the form ($\text{CaO}-\text{Fe}_2\text{O}_3-\text{H}_2\text{O}$).

A hydrated calcium ferrite of the form (C_3FH_6) is comparatively more stable. This hydrated product also does not contribute anything to the strength. The hydrate of (C_4AF) shows a comparatively higher resistance to the attack of sulphates than the hydrates of calcium Aluminate.

Heat of Hydration:

The compounds of Portland cement are non equilibrium products of high temperature reactions and are therefore in a high-energy state. When cement is hydrated, the compounds react with water to acquire stable, low-energy states and the process is accompanied by the release of energy in the form of heat. In other words, the hydration reactions of portland cement compounds are exothermic. The significance of heat of cement hydration in concrete technology is manifold. The heat of hydration can sometimes be a hindrance (e.g., mass concrete structures), and at other times a help (e.g., winter concreting when ambient temperatures may be too low to provide the activation energy for hydration reactions).

In general, on mixing cement with water, a rapid heat evolution (ascending portion of peak A) lasting a few minutes occurs. This probably represents the heat of solution of aluminates and sulfates. This initial heat evolution ceases quickly (descending portion of peak A) when the solubility of aluminates is depressed in the presence of sulfate in the solution. The next heat evolution cycle, culminating in the second peak after about 4 to 8 h of hydration for most portland cements, represents the heat of formation of ettringite (ascending portion of peak B).the heat evolution period includes some heat of solution due to C_3S and heat of formation of C-S-H. The paste of a properly retarded cement will retain much of its plasticity before the commencement of this heat cycle and will stiffen and show the initial set (beginning of solidification) before reaching the apex at B, which corresponds to the final set (complete solidification and beginning of hardening).

The hydration of Portland cement involves exothermic reactions, and the hydration operation release heat which can be illustrated in Figure

(2). The progress of the reactions can be monitored using the technique of isothermal conduction calorimetry.

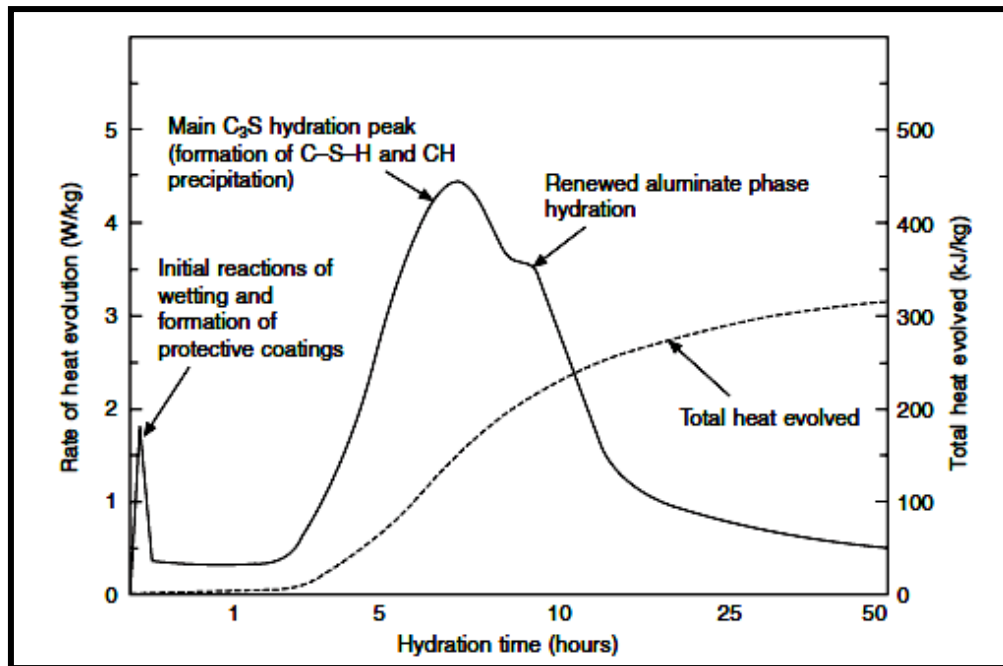


Figure (2): Heat of Hydration of a Cement Paste Determined by Conduction Calorimetry at (20°C).

The actual value of the heat of hydration depends on:

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 =

$$136(C3S) + 62(C2S) + 200(C3A) + 30(C4AF)$$

Where, the terms in brackets denote the percentage by mass of the individual compounds in cement. Because in the early stages of hydration the different compounds hydrate at different rates, the rate of heat

evolution, as well as the total heat depends on the compound composition of the cement.

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:

- Rapid hardening Portland cement.
- Ordinary Portland cement.
- Modified Portland cement.
- Sulfate resistant Portland cement.
- 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.

False setting

It is abnormal premature stiffening of cement within a few minutes of mixing with water. – It differs from **flash set** in that:

- No appreciable heat is evolved.

- Remixing the cement paste without addition of water restores plasticity of the paste until it sets in the normal manner and without a loss of strength.

1- Dehydration of gypsum – when interground with too hot a clinker - formed:

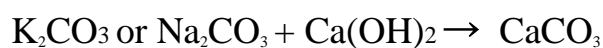
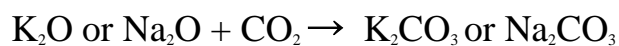
- Hemihydrates ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) – when temperature between $100-190^\circ\text{C}$

- or anhydrite (CaSO_4) - when temperature $>190^\circ\text{C}$

And when the cement is mixed with water these hydrate to form gypsum, with a result stiffening of the paste.

2- Reaction of alkalis of the cement

During bad storage – alkalis in the cement react with CO_2 (in the atmosphere) to form alkali carbonates, which they react with $\text{Ca}(\text{OH})_2$ liberated by the hydrolysis of C_3S to form CaCO_3 . This precipitates and induces a rigidity of the paste.



3- Activation of C_3S subjected to wet atmosphere

During bad storage – water is absorbed on the grains of cement (the water stick on their surfaces) and activates them, and these activated surfaces can combine very rapidly with more water during mixing: this rapid hydration would produce false set.

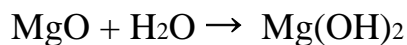
Flash setting: Occurs when there is no gypsum added or exhausting the gypsum (added with little amount), so C_3A reacts violently with water causing liberation high amount of heat causing rapid setting of cement, and leading to form porous microstructure that the product of hydration of the other compounds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

Soundness of cement

The cement considers unsound if it undergo a large change in volume (expansion) – that cause cracking of hardened cement paste when it is under condition of restraint.

2- Free MgO

Cement can also be unsound due to the presence of MgO, which reacts with water in a manner similar to CaO. However, only periclase, that is, 'dead-burnt' crystalline MgO, is deleteriously reactive, and MgO present in glass is harmless, because it hydrates quickly transforming to the stable state in the hardened paste.



Up to about 2 per cent of periclase, (by mass of cement) combines with the main cement compounds, but excess periclase generally causes expansion and can lead to slow disruption.

3- Calcium sulfates (gypsum)

Gypsum added to the clinker during its grinding in order to prevent flash set, but if gypsum is present in excess of the amount that can react with C₃A during setting, unsoundness is in the form of a slow expansion will result.

Fineness of cement:

The last step in the manufacture of cement is the grinding of clinker mixed with gypsum. Because hydration starts at the surface of the cement particles, it is the total surface area of cement that represents the material available for hydration. Thus, the rate of hydration depends on the fineness of the cement particles.

The high fineness is necessary for:

1. Rapid development of strength, as shown in the figure below; although the long-term strength is not affected. A higher early rate of hydration means, of course, also a higher rate of early heat evolution

2. To cover surfaces of the fine aggregate particles at better manner – leading to better adhesion and cohesion between cement mortar constituents.
3. To improve the workability of the concrete mix, but it will increase the amount of water required for the standard consistency.
4. To reduce the water layer that separate on the mixture surface due to bleeding, as shown in the figure below.

The disadvantage of high fineness, include:

1. The cost of grinding to a higher fineness is considerable.
2. The finer the cement the more rapidly it deteriorates on exposure to the atmosphere during bad storage.
3. Finer cement increases the surface area of its alkalis – leads to stronger reaction with alkali-reactive aggregate – cracks and deterioration of concrete.
4. Finer cement exhibits a higher shrinkage and a greater proneness to cracking.
5. An increase in fineness increases the amount of gypsum required for proper retardation because, in finer cement, more C_3A is available for early hydration (due to the increase of its surface area).

Capillary pores:

At any stage of hydration, the capillary pores represent that part of the gross volume which has not been filled by the products of hydration.

Because these products occupy more than twice the volume of the original solid phase (i.e. cement) alone, the volume of the capillary system is reduced with the progress of hydration.

Thus the capillary porosity of the paste depends on:

- The water/cement ratio of the mix

When w/c ratio > 0.38 – The gel volume is not enough to fill all the available voids.

- The degree of hydration, which influence by the type of cement.

Gel pores:

- The gel pores are interconnected interstitial spaces between the gel particles.
- The gel pores are much smaller than the capillary pores: Less than 2 or 3 nm in nominal diameter. This is only one order of magnitude greater than the size of molecules of water. For this reason, the vapour pressure and mobility of adsorbed water are different from the corresponding properties of free water.
- The gel pores occupy about 28 per cent of the total volume of gel (gel particles + gel pores).
- The actual value is characteristic for a given cement but is largely independent of the water/cement ratio of the mix and of the progress of hydration. This would indicate that gel of similar properties is formed at all stages and that continued hydration does not affect the products already in existence. Thus, as the total volume of gel increases with the progress of hydration, the total volume of gel pores also increases. On the other hand, as mentioned earlier, the volume of capillary pores decreases with the progress of hydration.

Water held in hydrated cement paste:

The hydrated cement paste – contains sub-microscopic pores – that can absorb water from the ambient area. The actual water content of the paste depends on the ambient humidity.

Capillary pores, because of their comparatively large size, empty when the ambient relative humidity falls below about 45 per cent, but water is

adsorbed in the gel pores even at very low ambient humidities, because it is too small compared with the capillary pores.

We can thus see that water in hydrated cement is held with varying degrees of firmness:

- **Free water** – present in the capillary pores – with weak firmness, and evaporate quickly leaving the paste.
- **Chemically combined water** – form a definite part of the hydrated compounds.
- **Gel water** – present in gel pores – part of it is held by the surface force of the gel particles - It is known as **the adsorbed water**.

There is no technique available for determining how water is distributed between these different states, nor is it easy to predict these divisions from theoretical considerations as the energy of binding of combined water in the hydrate is of the same order of magnitude as the energy of binding of the adsorbed water.

A convenient division of water in the hydrated cement, necessary for investigation purposes, though rather arbitrary, is into two categories:

- **Evaporable water** – includes water in the capillary pores and some water in the gel pores.
- **Non-evaporable water** – includes nearly all chemically combined water and also some water not held by chemical bonds.

The amount of non-evaporable water increases as hydration proceeds. In **well-hydrated cement**, the non-evaporable water is about **18 percent** by mass of the anhydrous material; this proportion rises to about **23 percent** in **fully hydrated cement**. The evaporable water can be measured from – loss in weight of cement paste sample through drying at 105°C to the equilibrium state.

Setting:

Setting refers to a change from a fluid to a rigid stage:

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

The **stages of setting** include:

- Initial setting
- Final setting

It is important to distinguish setting from **hardening**, which refers to the gain of strength of a set cement paste.

The two first to react are C_3A and C_3S .

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.

There are four main stages during setting

- **First stage:**

- 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.

- **Second stage (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.

- **Third stage:**

- 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.

- **Fourth stage:**

- 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.

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