

Chapter One

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 washmill. **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 analyze chemically to check the achievement of the required chemical composition, and if necessary changing the mix constituents 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.

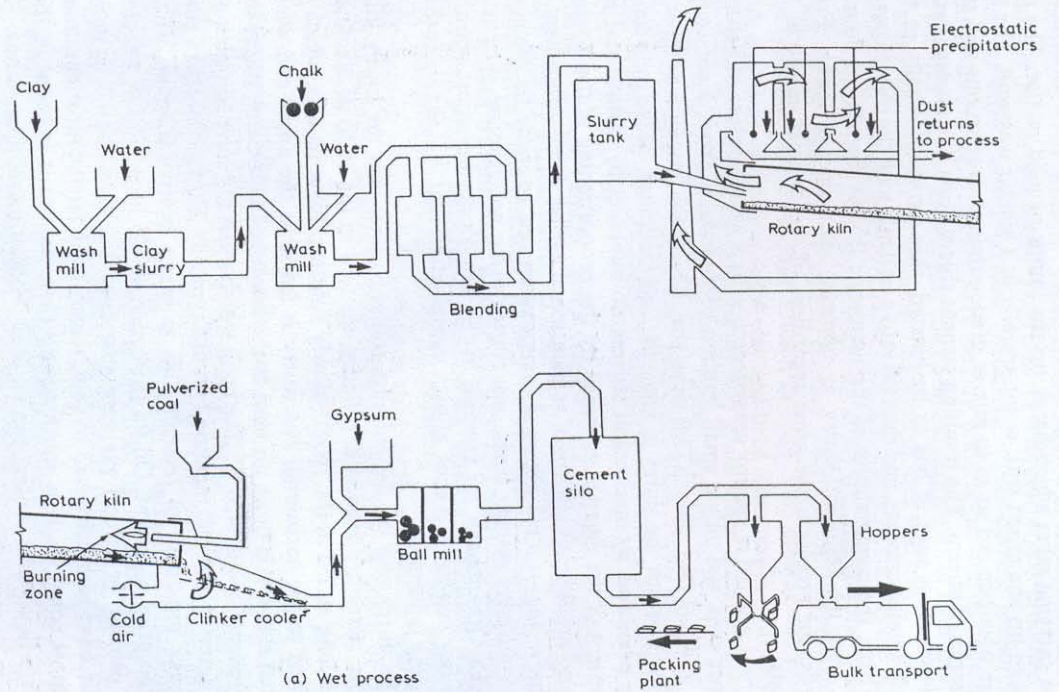
The slurry, in its movement down the kiln, encounters a progressively higher temperature. At first, the water is driven off and CO₂ is liberated; further on, the dry material undergoes a series of chemical reactions until finally, in the hottest part of the kiln, some 20 to 30% of the material becomes 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 subsequent operations are the same as in the wet process of manufacture.



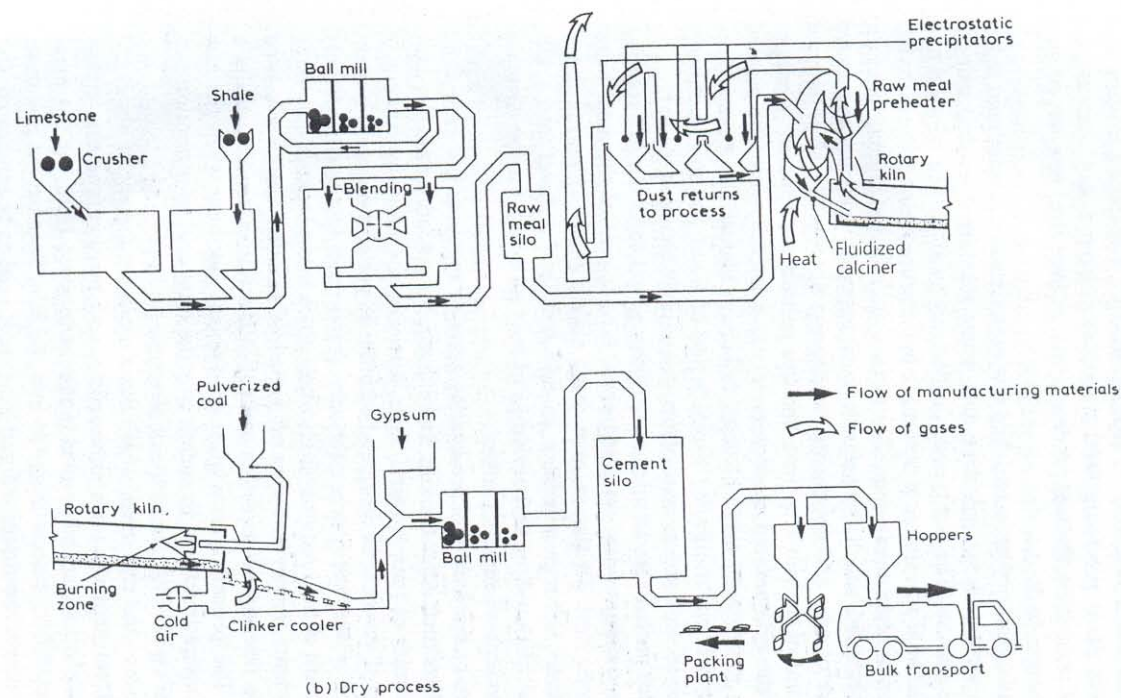


Fig. 1.1 Diagrammatic representation of: (a) the wet process and (b) the dry process of manufacture of cement

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.

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

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 $3\text{CaO}.\text{SiO}_2 - (\text{C}_3\text{S})$
- Dicalcium silicate $2\text{CaO}.\text{SiO}_2 - (\text{C}_2\text{S})$
- Tricalcium aluminate $3\text{CaO}.\text{Al}_2\text{O}_3 - (\text{C}_3\text{A})$
- Tetracalcium aluminoferrite $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3 - (\text{C}_4\text{AF})$

Where each oxide symbol with one letter:

$\text{CaO} - \text{C}$

$\text{SiO}_2 - \text{S}$

$\text{Al}_2\text{O}_3 - \text{A}$

$\text{Fe}_2\text{O}_3 - \text{F}$

$\text{H}_2\text{O} - \text{H}$

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

$$\text{C}_3\text{S} = 4.07 (\text{CaO}) - 7.6 (\text{SiO}_2) - 6.72 (\text{Al}_2\text{O}_3) - 1.43 (\text{Fe}_2\text{O}_3) - 2.85 (\text{SO}_3)$$

$$\text{C}_2\text{S} = 2.87(\text{SiO}_2) - 0.754 (\text{C}_3\text{S})$$

$$\text{C}_3\text{A} = 2.65 (\text{Al}_2\text{O}_3) - 1.69 (\text{Fe}_2\text{O}_3)$$

$$\text{C}_4\text{AF} = 3.04 (\text{Fe}_2\text{O}_3)$$

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 , C_3S decomposes slowly **but**, if cooling is not too slow, C_3S 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. **SO₃** by 2.5% when **C₃A** \leq 7%, and by 3% when **C₃A** $>$ 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 ₂ O ₃	3-8
Fe ₂ O ₃	0.5-6
MgO	0.5-4
Alkalis (as Na ₂ O)	0.3-1.2
SO ₃	2.0-3.5

Typical compound composition in ordinary Portland cement

Compound	Content, %
C ₃ S	54
C ₂ S	17
C ₃ A	11
C ₄ AF	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.

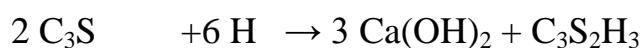
Insoluble residue

It is that part of cement sample that is insoluble in HCl. It comes from the unreacted 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.

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 (C_3S and C_2S) and aluminates (C_3A and C_4AF) 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 C_3S hydration equation



The reaction of C_3S with water continue even when the solution is saturated with lime and the resulted amounts of lime precipitate in crystals form $Ca(OH)_2$.

Calcium silicate hydrate → remains stable when it is in contact with the solution saturated with lime.

Calcium silicate hydrate → hydrolyzed when being in water – some of lime form, and the process continues until the water saturate with lime.

If the calcium silicate hydrate remains in contact with water → it will leave the hardened compound only as hydrated silica due to the hydrolysis of all of the lime.

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 main hydrates of the hydration process are:

- **Calcium silicates hydrate**, including hydrated products of C_3S (not pure) named as **Alite**, and C_2S (not pure) named as **Belite**.
- **Tricalcium aluminate hydrate**
- **C_4AF** hydrates to tricalcium aluminate hydrate and calcium ferrite $CaO.Fe_2O_3$ in amorphous form.

Since calcium silicates (C_3S and C_2S) – are the main cement compounds (occupies about 75% of cement weight) – they are responsible for the final strength of the hardened cement paste.

With time:

- The rate of hydration decreases continuously.
- The size of unhydrated cement particles decrease. For instance, after 28 days in contact with water, grains of cement have been found to have hydrated to a depth of only 4 μm , and 8 μm after a year.

This is due to:

- 1) Accumulation of hydration products around the unhydrated cement grains which lead to prevent water from channeling to them.
- 2) Reduction of the amount of water either due to chemical reaction or evaporation.
- 3) Reduction of the amount of cement due to reaction.

The progress of hydration of cement can be determined by different means:

- The measurement of the amount of Ca(OH)_2 in the paste resulted from the hydration of the silicates.

$$2 \text{C}_3\text{S} + 6\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + 3 \text{Ca(OH)}_2$$

$$2 \text{C}_2\text{S} + 4\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + \text{Ca(OH)}_2$$
- The heat evolved by hydration.
- The specific gravity of the paste.
- The amount of chemically combined water.
- The amount of unhydrated cement present (using X-ray quantitative analysis).
- Also indirectly from the strength of the hydrated paste.

Tricalcium aluminate hydrate and the action of gypsum

The amount of C_3A present in most cements is comparatively small but its behaviour and structural relationship with the other phases in cement make it of interest. The tricalcium aluminate hydrate forms a prismatic dark interstitial material in the form of flat plates individually surrounded by the calcium silicate hydrate.

The reaction of pure C_3A with water is very violent with evolution of large amount of heat, forming calcium aluminates hydrate in the form of leaf hexagonal crystals. In Portland cement, this reaction leads to immediate stiffening known as "flash setting".

Gypsum, added to the clinker through grinding process cause delaying the reaction of C_3A with water by its reaction with C_3A to form insoluble calcium sulfoaluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO} \cdot 30-32\text{H}_2\text{O}$) - ettringite - around C_3A particles, which permits enough time for the hydration of C_3S that its reaction is slower than C_3A and permits the occurring of natural setting. But eventually tricalcium aluminate hydrate is formed, although this is preceded by a metastable $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO} \cdot 12\text{H}_2\text{O}$, produced at the expense of the original high-sulfate calcium sulfoaluminate.

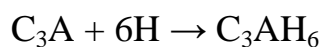
The reaction of gypsum with C_3A continues until one of them exhausted, while C_3S continue in hydration.

- If C_3A exhausted before gypsum

The surplus gypsum \rightarrow expand \rightarrow become an agent assist the disruption and deterioration of cement paste.

- If gypsum exhausted before C_3A

The remaining C_3A begins in hydration:



C_3AH_6 is stable –cubical crystals- with high sulfate resistance.

Calcium aluminate hydrate – Be at many forms before transforming to the stable state (C_3AH_6). It is probably forming hexagonal crystals (C_4AH_8 , C_4AH_{10} , C_4AH_{12}) before the cubical crystals.

When the hexagonal crystals expose to sulfates (inside concrete from sand **or** external from soil or ground water) → react with it forming calcium sulfoaluminate → with increase in volume, depending on the amount of remaining aluminates and the concentration of sulfates → crack and deteriorate of the hardened concrete.

The transformation of calcium aluminates hydrate from the metastable hexagonal form to the stable cubical form is accompanied with – change in the density and size of the crystals – leading to decrease in the late ages strength of the cement paste due to

- lose the adhesion and cohesion in the microstructure
- increase the porosity of the hardened cement paste.

The presence of C_3A in cement is undesirable: it contributes little to the strength of cement except at early ages (1-3 days) and, when hardened cement paste is attacked by sulfates, expansion due to the formation of calcium sulfoaluminate from C_3A may result in a disruption of the hardened paste.

But it is useful in the cement industry – work as flux material – reduce the temperature needed to form the clinker. Also it facilitates the combination of lime with silica.

C₄AF compound

Gypsum reacts with C_4AF to form calcium sulfoaluminates and calcium sulfoferrite.

C_4AF – work as flux material and also it accelerates the hydration of silicates.

Using the optimum percentage of gypsum is very important because:

- It regulates the speed of the chemical reactions in the early ages.
- Prevent the local concentration of the hydration products.

The necessary gypsum content increase with the increase of:

- C_3A content in the cement.
- Alkalis content in the cement.
- Fineness of cement.

Iraqi specification No. 5 limits the maximum gypsum content (expressed as the mass of SO_3 present) to be not more than 2.5% when $C_3A \leq 7\%$ and 3% when $C_3A > 7\%$.

Calcium silicates hydrate**C₃S**

- C₃S + water →
- lime and silica ions in the solution with molecular weight of 3:1
 - Ca(OH)₂ crystals
 - Calcium silicate hydrate gel (**tobermorite**)

Hydration of C₃S – take about one year or more

This initial gel form an external layer over C₃S causing the delay of the reaction. After few hours, this initial C-S-H undergo hydrolysis to form the second product of the gel CSH I with C:S equal 1.5 then form the stable C-S-H II form with C:S equal 1.4-1.6.

The full hydration of C₃S can be expressed approximately by the following equation:

**C₂S**

There are three main crystal forms of C₂S (α , β , γ) but the β -form is the only one occurred in the Portland cement and it react slowly with water.

- Its reaction is slower than C₃S.
- The amount of Ca(OH)₂ from its hydration is less.

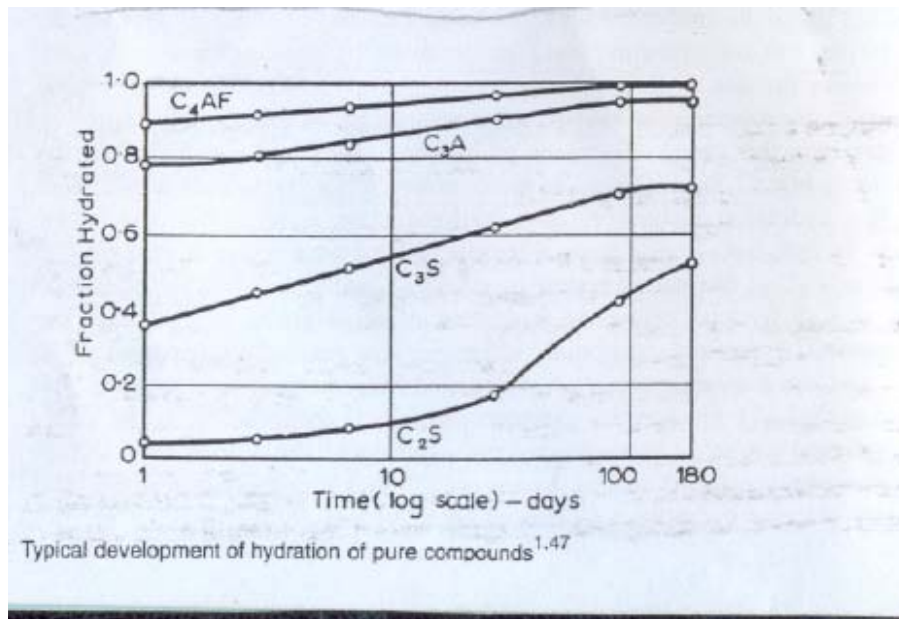
Its formed gel is similar to that produced from C₃S, but there is difference in the route of the chemical reactions between the two compounds – the lime: silica during the hydration of C₂S differs than that formed during the hydration of C₃S. It is in the initial product formed as external layer at the surface about 2, and after 12 hours the initial product transform to CSH I with C:S equal 1.1-1.2 then form the stable C-S-H II form with C:S equal 1.65-1.8 at 25°C.

- Hydration of C₂S – takes more than 4 years.

The full hydration of C₂S can be expressed approximately by the following equation:



The rates of hydration of the two compounds are different as shown in the figure below:



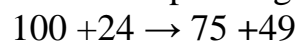
The gel formed after the completion of hydration of the two compounds is $\rightarrow C_3S_2H_3$ – Tobermorite.

C_3S and C_2S – require approximately the same amount of water for hydration, but C_3S produces more than twice as much $Ca(OH)_2$ as is formed by the hydration of C_2S , as shown in the equations below:

For C_3S hydration



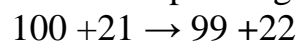
The corresponding masses involved are:



For C_2S hydration



The corresponding masses involved are:



Setting

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

Cement + water \rightarrow cement paste \rightarrow lose its plasticity gradually \rightarrow when it lose its plasticity completely \rightarrow 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 C_3S 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 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**

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.

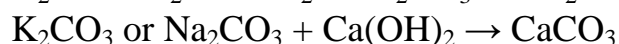
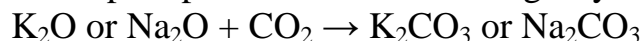
Causes of false setting

- 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 $100\text{-}190^\circ\text{C}$
 - 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 adsorbed 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.

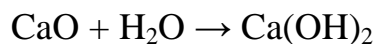
Soundness of cement

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.

Causes of expansion

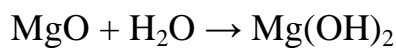
1- Free lime CaO

If the raw materials fed into the kiln contain more lime that can combine with the acidic oxides, or if burning or cooling are unsatisfactory, the excess lime will remain in a free condition. This hard-burnt lime hydrates only very slowly and, because slaked lime occupies a larger volume than the original free calcium oxide, expansion takes place. Cements which exhibit this expansion are described as unsound.



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.

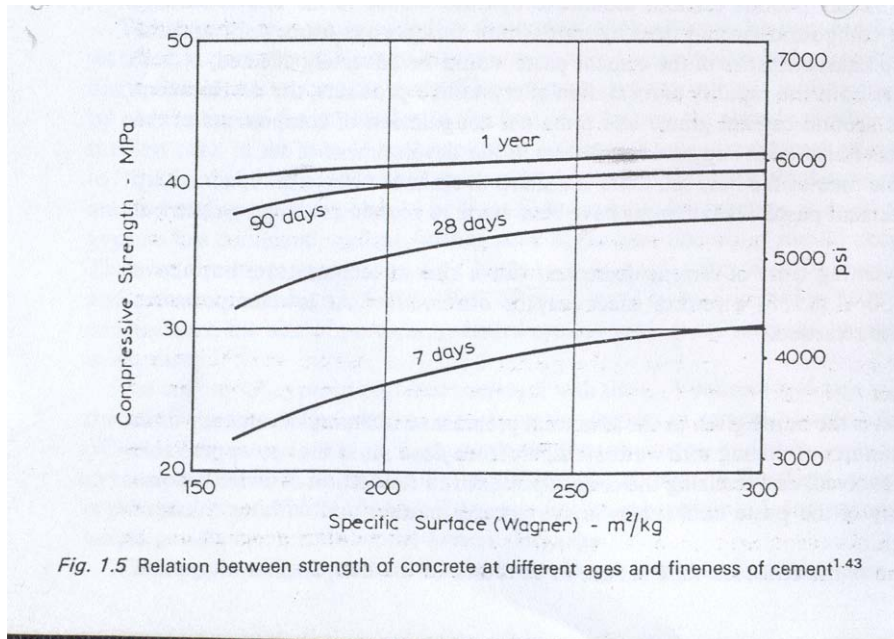
Fineness of cement

The last step in the manufacture of cement is the grinding of clinker mixed with gypsum.

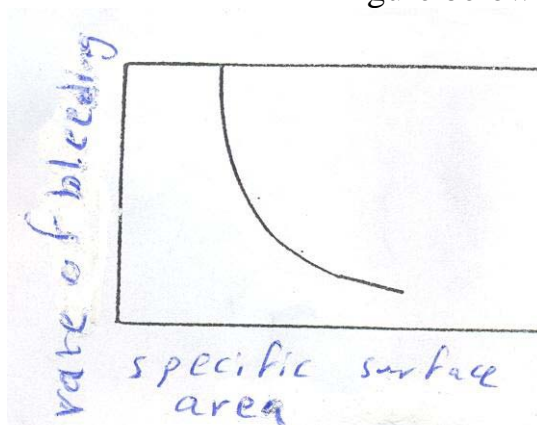
Because hydration starts at the surface of the cement particles, it is the total surface area of cement that represents the material available for hydration. Thus, the rate of hydration depends on the fineness of the cement particles.

The high fineness is necessary for:

- 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



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



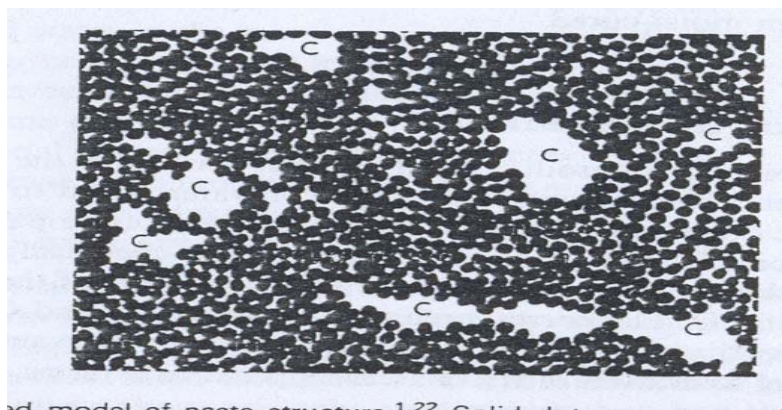
The disadvantage of high fineness, include:

- The cost of grinding to a higher fineness is considerable.

- The finer the cement the more rapidly it deteriorates on exposure to the atmosphere during bad storage.
- Finer cement increases the surface area of its alkalis – leads to stronger reaction with alkali-reactive aggregate – cracks and deterioration of concrete.
- Finer cement exhibits a higher shrinkage and a greater proneness to cracking.
- 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).

Structure of hydrated cement

At any stage of hydration, the hardened paste consists of very poorly crystallized hydrates of the various compounds (calcium silicates hydrate, tricalcium aluminates hydrate and calcium ferrite), referred to collectively as gel, of crystals of $Ca(OH)$ produced from the hydration of the silicates, some minor components, unhydrated cement, and the residue of the water-filled spaces in the fresh paste. These voids are called **capillary pores** but, within the gel itself, there exist interstitial voids, called **gel pores**. The nominal diameter of gel pores is about 3 nm while capillary pores are one or two orders of magnitude larger. There are thus, in hydrated paste, two distinct classes of pores represented diagrammatically in the figure below.



Simplified model of paste structure. Solid dots represent gel particles; interstitial spaces are gel pores; spaces such as those marked C are capillary pores

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.

Capillary pores:

- cannot be viewed directly but their median size was estimated to be about $1.3 \mu\text{m}$.
- They vary in shape and form an interconnected system randomly distributed throughout the cement paste.
- These interconnected capillary pores are mainly responsible for the permeability of the hardened cement paste and for its vulnerability to cycles of freezing and thawing.

However, hydration increases the solid content of the paste and in mature and dense pastes - the capillaries can become blocked by gel and segmented so that they turn into capillary pores interconnected solely by the gel pores.

The absence of continuous capillaries is due to:

- Using a suitable water/cement ratio
- Sufficiently long period of moist curing

The degree of maturity required for different water/cement ratios for ordinary Portland cements is indicated in figure below.

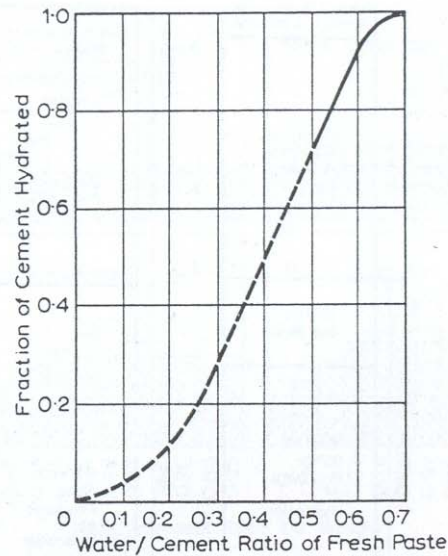


Fig. 1.12 Relation between the water/cement ratio and the degree of hydration at which the capillaries cease to be continuous^{1,26}

It can be seen that the estimated required time for maturity of cement paste are:

w/c ratio	time
0.4	3 days
0.7	One year
More than 0.7	Not possible

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 per cent** by mass of the anhydrous material; this proportion rises to about **23 per cent** 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.

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.

Because the thermal conductivity of concrete is comparatively low - it acts as an insulator, and in the interior of a large concrete mass, hydration can result in a large rise in temperature. At the same time, the exterior of the concrete mass loses some heat so that a steep temperature gradient may be established and, during subsequent cooling of the interior, serious cracking may result due to the generated stresses.

At the other extreme, the heat produced by the hydration of cement may prevent freezing of the water in the capillaries of freshly placed concrete in cold weather, and a high evolution of heat is therefore advantageous.

The most common method of determining the heat of hydration is by measuring the heats of solution of unhydrated and hydrated cement in a mixture of nitric and hydrofluoric acids: the difference between the two values represents the heat of hydration. This method is described in BS 4550:Section 3.8:1978, and is similar to the method of ASTM C 186-94.

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.

For practical purposes, it is not necessarily the total heat of hydration that matters but the rate of heat evolution. The same total heat produced over a longer period can be dissipated to a greater degree with a consequent smaller rise in temperature.

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:

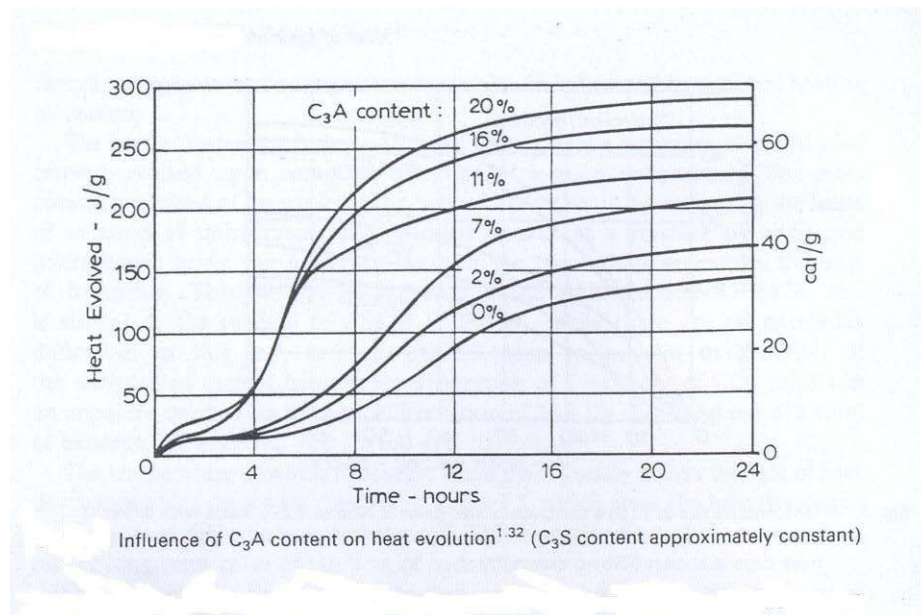
$$\text{Heat of hydration of 1 g of cement} = 136(C_3S) + 62(C_2S) + 200(C_3A) + 30(C_4AF)$$

where the terms in brackets denote the percentage by mass of the individual compounds in cement.

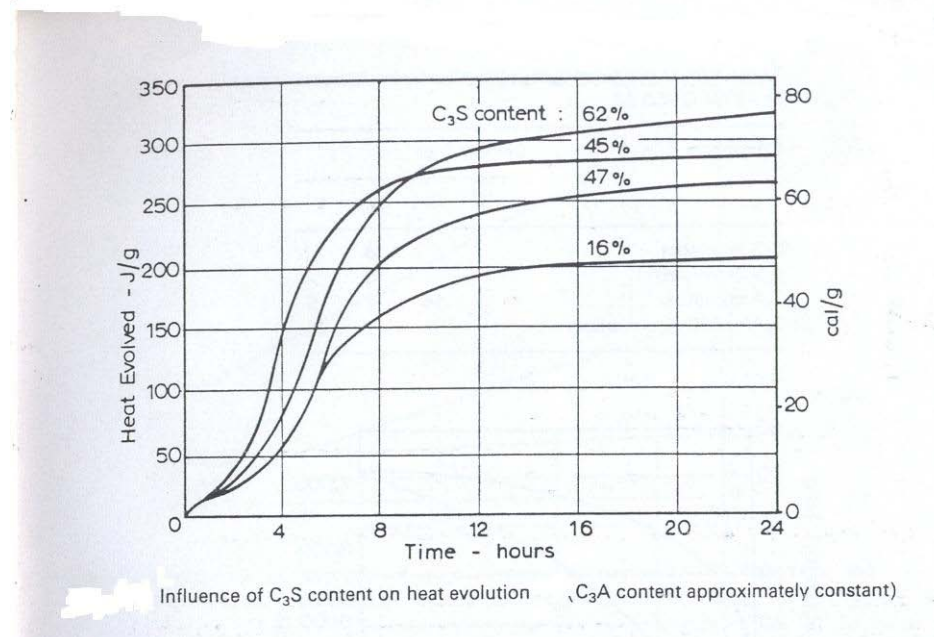
Because in the early stages of hydration the different compounds hydrate at different rates, the rate of heat evolution, as well as the total heat depends on the compound composition of the cement.

It follows that by reducing the

Proportions of the compounds that hydrate most rapidly (C_3A and C_3S) the high rate of heat evolution in the early life of concrete can be lowered. The effect of C_3A on heat of hydration of cement is shown in the Fig. below.



The effect of C_3S on heat of hydration of cement is shown in the Fig. below.



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.

Influence of the compound composition on properties of cement

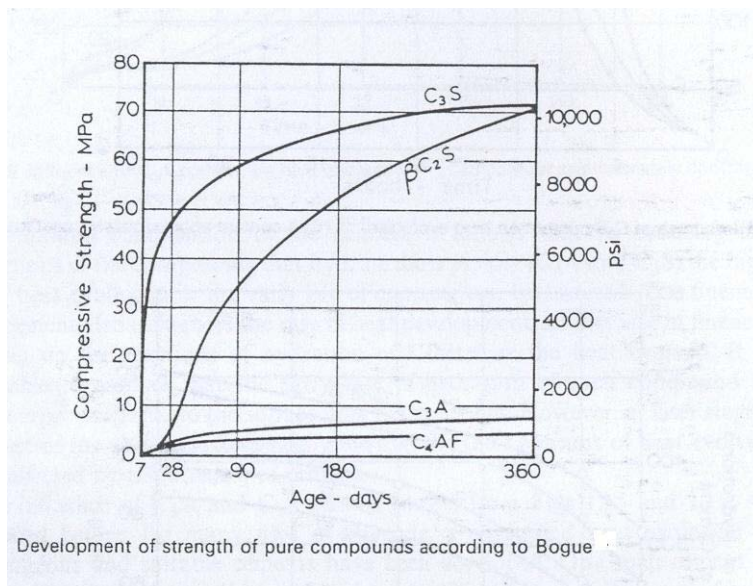
Main compounds

C₃S and C₂S – are the most important compounds – responsible for strength.

C₃S – contributes most to the strength development during the first four weeks.

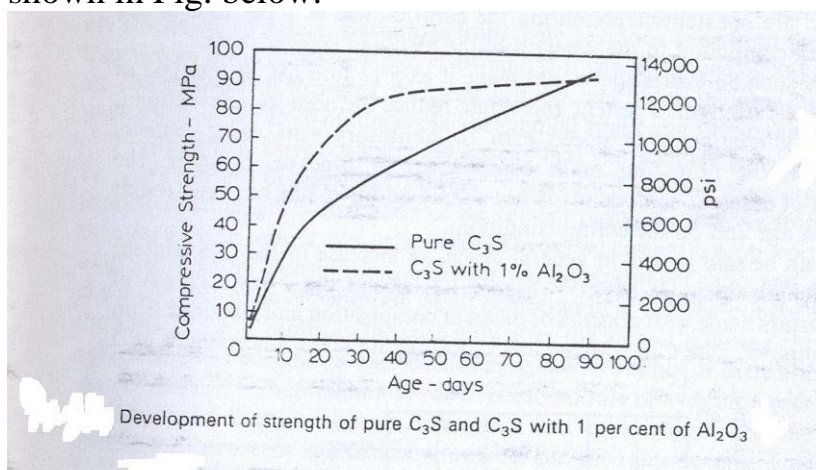
C₂S – influences the gain in strength from 4 weeks onwards.

At the age or about one year, the two compounds, contribute approximately equally to the ultimate strength.



Calcium silicates appear in commercial cements in 'impure' form.

These impurities may strongly affect the rate of reaction and of strength development of the hydrates. For instance, the addition of 1 per cent of Al_2O_3 to pure C_3S increases the early strength of the hydrated paste, as shown in Fig. below.



This increase in strength probably results from activation of the silicate crystal lattice due to introduction of the alumina into the crystal lattice and rearranges its structure.

C_3A contributes to the strength of the cement paste at one to three days, and possibly longer, but causes retrogression at an advanced age, particularly in cements with a high C_3A or ($\text{C}_3\text{A} + \text{C}_4\text{AF}$) content.

The role of C_4AF in the development of strength of cement is not clear till now, but there certainly is no appreciable positive contribution. It is likely that colloidal hydrated $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ is deposited on the cement grains, thus delaying the progress of hydration of other compounds.

From the knowledge of the contribution to strength of the individual compounds present, it might be thought possible to predict the strength of

cement on the basis of its compound composition. This would be in the form of an expression of the type:

$$\text{Strength} = a(C_3S) + b(C_2S) + c(C_3A) + d(C_4AF)$$

where the symbols in brackets represent the percentage by mass of the compound, and a, b, etc. are constants representing the contribution of 1 per cent of the corresponding compound to the strength of the hydrated cement paste.

Alkalis

Tests on the influence of alkalis have shown that the increase in strength beyond the age of 28 days is strongly affected by the alkali content: the greater the amount of alkali presents the lower the gain in strength. The poor gain in strength between 3 and 28 days can be attributed more specifically to water-soluble K_2O present in the cement. On the other hand, in the total absence of alkalis, the early strength of cement paste can be abnormally low.

The alkalis are known to react with the so-called alkali-reactive aggregates – the product of reaction accompanied with increase in volume – leads to cracking of concrete mass, and cements used under such circumstances often have their alkali content limited to 0.6 per cent (measured as equivalent Na_2O). Such cements are referred to as low-alkali cements.