

CHAPTER IV

FORMATION OF CEMENT

All the compounds present in Portland cement clinker are anhydrous, but when brought into contact with water, they are all attacked or decomposed forming hydrated compounds of different composition and crystallinity and influence the engineering properties of the final product-concrete-in different ways. Supersaturated and unstable solutions are formed temporarily, but these gradually deposit their excess solids and tend to come into equilibrium with the hydrate compounds produced. The rate of attack, and the degree of temporary supersaturation of the solutions, are determined by the physical state of the cement compounds as well as by their chemical nature. Since the original anhydrous compounds cannot exist in equilibrium with aqueous solutions the ultimate result of the action of water must be complete hydration. We cannot speak of the solubility of, for example, tricalcium or dicalcium silicate in water since it is not a definite physical quantity, there is no aqueous solution in which these compounds can be placed and remain in equilibrium, or from which they would separate on evaporation. The hydrated compounds, on the other hand, can exist permanently in contact with certain solutions, though in many cases they form what are known as incongruent solutions. This will be the cause of the complete decomposition of the hydration products of cement when they are continually extracted with water and will be one of the important factors in deterioration, under certain conditions,

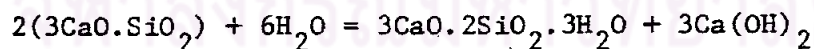
of concrete structures.

The nature of the chemical action of water on cement compounds may perhaps be more clearly illustrated if we first consider the hydration of C_3S .

4.1 Hydration of Individual Cement Compound

4.1.1 Tricalcium silicate:

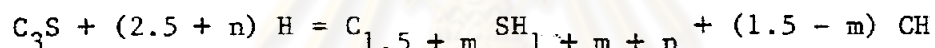
When finely ground C_3S is mixed with water, hydration commences quickly and both lime and silica pass into solution initially in the same molecular ratio 3:1 as in the anhydrous compound. The concentration of lime in solution increases steadily while that of silica rapidly decreases. Crystals of calcium hydroxide soon appear together with a gelatinous or nearly amorphous hydrated calcium silicate. Complete hydration cannot be obtained under periods of a year or more unless the C_3S is very finely divided and the mix reground at intervals to expose fresh surfaces to the water. Otherwise the product obtained shows unattacked cores of C_3S surrounded by a layer of hydrated silicate which, being relatively impervious to water, renders further attack slow. At complete hydration the reaction can approximately be represented by the equation



but this simple equation does not bring out the complexities of the reaction. The immediate product formed in pastes on mixing has a $CaO:SiO_2$ ratio near to 3. This forms as a coating on the C_3S surfaces and retards the reaction. After a few hours, dissolution or splitting off of this initial product results in an acceleration of the hydration and the

formation as the second product of a C-S-H gel of lower $\text{CaO}:\text{SiO}_2$ ratio, 1.5 or less |C-S-H (I)|. This is followed by formation of a third stable product |C-S-H (II)|. The second product may be a poorly crystallised C-S-H (I) and the third C-S-H (II) or a closely related product. The completely hydrated silicate, which may well be a heterogeneous material containing both these latter products, has a $\text{CaO}:\text{SiO}_2$ ratio of about 1.4 to 1.6. This ratio increases somewhat as the water: solid ratio of the mix is decreased.

The hydration reaction is thus more correctly represented in a generalised form by the equation:

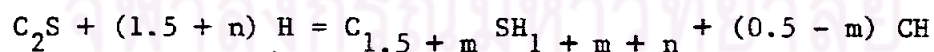


where CH represents $\text{Ca}(\text{OH})_2$ and H represents the water retained in drying to equilibrium with the vapour pressure of ice at -78.5°C .

The action does not stop when the solution is saturated with calcium hydroxide, but hydration continues and the further lime liberated by the reaction is deposited as crystals of calcium hydroxide. The hydrated silicate formed remains stable in contact with the saturated lime solution, but if it is placed in water it undergoes hydrolysis, liberating some lime into solution until the concentration is raised to the value required to stabilise it. Continued extraction with water of the hydrated calcium silicate eventually leaves a solid composed only of hydrated silica, all the lime having been dissolved and removed whilst very little of the silica is dissolved.

4.1.2 Dicalcium silicate:

There are four main polymorphic forms of the C_2S , γ , β , α' and α of which only the β or occasionally the α' or γ form occurs in Portland cement. Nurse²⁷ has shown that γ is almost inert, that α' gives very poor strength and that α is non-hydraulic. The β form is only slowly attacked by water and even after some weeks the original crystals show only a surface coating of an amorphous hydrated silicate, the thickness of which slowly increases with the passage of time. Although the reaction is considerably slower than with C_3S and substantially less calcium hydroxide is produced, the C-S-H gels produced are of the same type as those from C_3S . There are, however, differences in the course of the two reactions. With C_2S pastes the initial product, formed as a surface coating, has a $CaO:SiO_2$ ratio close to 2. Within twelve hours or so this converts into a low-lime product related to C-S-H (I) and the molar ratio drops to a minimum value between 1.1 and 1.2. A stable final product related to C-S-H (II) is then gradually formed and the molar ratio gradually increases reaching a final value at 25°C of 1.65 to 1.8 after a year or so. A more generalised equation apply to hydration in pastes at any age or water: solid ratio is



The rate of hydration and the strength developed by βC_2S depends on the nature of the stabilisers. At ordinary temperature γC_2S is attacked by water more slowly than the β form but eventually a hydrated silicate is formed.

4.1.3 Tricalcium aluminater:

Finely ground C_3A reacts very rapidly with water, though apparently less so in a saturated lime solution. C_3AH_6 can also be formed very rapidly when C_3A is mixed with a limited amount of water at normal temperatures to form a plastic mass, since there is considerable heat evolution and the temperature of the material rises, favouring the formation of C_3AH_6 . Complete hydration is only reached slowly owing to the protection afforded to the unhydrated cores by the hydrate surrounding them.

4.1.4 Tetracalcium aluminoferrite:

Although the ferrite phase in Portland cement is not necessarily C_4AF as such. The rate of reaction of the C_4AF with water increases with the proportion of alumina in the aluminoferrite and C_4AF therefore though reacting quickly does so less rapidly than C_3A .

C_4AF reacts with water to form an amorphous hydrate which has not definitely been established and crystalline $C_3AH_6 \cdot Ca(OH)_2$ is not precipitated during the hydration of C_4AF . In saturated limewater, or in the presence of excess lime, the reaction of C_4AF is less rapid and rather different in that hydrated iron oxide/ αFe_2O_3 is not produced.

4.1.5 Calcium silicate hydrates:

The composition of the calcium silicate hydrate gels produced during the hydration of the anhydrous silicates changes during the period of the reaction and it also varies with the water: solid ratio of the mix and the temperature. The reaction product may be denoted as a C-S-H gel without implying any particular composition. More specific forms of the

gel are denoted as C-S-H (I) consisting of poorly crystallised foils or platelets with a tobermorite-like structure and $\text{CaO}:\text{SiO}_2$ molar ratio of 0.8 to 1.5 and C-S-H (II) with a fibrous structure and a molar ratio of 1.5 to 2.0. The C-S-H gels obtained in the hydration of C_3S or C_2S are very poorly crystallised products showing only a few of the x-ray diffraction lines of well crystallised tobermorites. They are commonly described as "tobermorite gels" but in view of the difficulty of precise identification the term C-S-H gels seems preferable. Though there is still some uncertainty regarding the $\text{CaO}:\text{SiO}_2$ ratio of the C-S-H in contact with a saturated lime solution. It is generally concluded that over a range of lime concentrations from about 0.05 gm CaO per litre up to close to saturation the C-S-H (I) is formed with a composition varying over the range $\text{CaO}_{0.8-1.5} \text{SiO}_2 \cdot \text{aq}$ ($\text{CaO}/\text{SiO}_2 = 0.8-1.5$) while in the region of lime saturation the C-S-H (II) with a composition $\text{CaO}_{1.5-2.0} \cdot \text{SiO}_2 \cdot \text{aq}$. ($\text{CaO}/\text{SiO}_2 = 1.5-2.0$) is formed. Since C-S-H (I) and (II) are so closely related in their structure and properties, their distinction is not easy and almost impossible at $\text{CaO}:\text{SiO}_2$ ratios near 1.5. The C-S-H (I) and C-S-H (II) are apparently both very closely related to tobermorite as described. The following is concluded and taken from a paper by Bogue and Lerch.³

The products of the reaction of water on C_3S , are crystalline CH and an amorphous C-S-H of composition approaching $2\text{CaO} \cdot \text{SiO}_2 \cdot x\text{H}_2\text{O}$. The β (beta) dicalcium silicate hydrates to approximately the same amorphous hydrated silicate (C-S-H), but only traces of crystalline calcium hydroxide (CH) have been observed.

The compounds containing alumina react rapidly with water to form a fluffy, crystalline, isotropic, hydrated calcium aluminate of a composition $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ (C_3AH_6).

The C_4AF reacts with water to form an amorphous hydrate, the composition of which has not definitely been established, and crystalline C_3AH_6 .

Gypsum reacts with the alumina that enters into solution, with the formation of crystalline calcium sulfoaluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$. This occasions a delay in the development of the crystalline hydrated tricalcium aluminate and so retards the initial set.

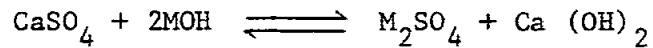
4.2 Hydration of Portland cement

From 4.1, the reactions of the individual cement compounds with water and the nature of the hydrated compounds that exist in the complex aqueous systems have been discussed. Now, integrate this knowledge into a picture of the reactions of cement itself.

The reaction of cement with water is in the first instance a reaction of the individual constituents. The C_3A and ferrite phases react quickly at first, as also does the C_3S , but the $\beta\text{-C}_2\text{S}$ reacts with water more slowly. The gypsum in cement also commences to dissolve rapidly, and the alumina compounds crystallise out as hydrated calcium aluminate and/or sulfoaluminate. The occurrence of calcium hydroxide plates and hexagonal prisms can also be observed, together with an apparently amorphous hydrated silicate covering the original grains.

Within a very short period of time, if not almost immediately,

after a cement is mixed with water, the liquid phase is essentially a solution of the hydroxides and sulphates of calcium, sodium and potassium tending towards the following equilibrium



where M is either K or Na or both. Only extremely small amounts of Al_2O_3 , SiO_2 and other oxides have been found to be present in the aqueous phase. At this time, both $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$ are present in the solid, and the solution is saturated, or even supersaturated, with respect to these compounds. Whilst solid $\text{Ca}(\text{OH})_2$ persists in hydrated Portland cement at all ages, the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is rapidly used up as an increasing amount of the almost insoluble hydrated calcium sulphoaluminate is formed, and eventually the sulphate is almost completely removed from solution, usually between about 10 and 24 hours after gauging the cement with water. Thereafter, the liquid phase in cement paste becomes a NaOH and/or KOH solution which is saturated or perhaps supersaturated, with respect to Calcium hydroxide, and in general the lime concentration continues to decrease gradually with slow further release of alkali from the cement. The alkalis exist in cement both as the sulphates which pass into solution rapidly and as components of the alumina and silica compounds from which they effectively dissolve as hydroxides. The reduced solubility of lime in the presence of alkali hydroxides, as well as the possible increased solubility of alumina and silica, may have some influence on the nature of the cement hydration products, but there is not at present sufficient information on the influence of alkalis on the cement hydration reactions.

It is now generally accepted that the immediate reaction of the

C_3A with gypsum during the hydration of cement leads to the formation of the high-sulphate compound first. This may well depend on the availability of calcium sulphate in the solution adjacent to the C_3A . In cement pastes of low water-cement ratio there may be a restricted mobility of ions in solution and, if local variations in solution concentration occur so that insufficient calcium sulphate is available in the solution near to the hydrating C_3A , then the low-sulphate sulphoaluminate will tend to form temporarily at an early age. On the other hand, if saturated solutions are established throughout the cement paste, it must be expected that the high-sulphate sulphoaluminate will form and persist until almost all the sulphate has been removed from the solution. At this point, and with further hydration of the C_3A , the high-sulphate sulphoaluminate will start to convert to the low-sulphate sulphoaluminate or to the hexagonal-plate solid solution. Once the limiting solid-solution composition is established any remaining C_3A will hydrate and convert to C_3AH_6 .

The C_4AF which reacts less instantaneously than the C_3A may be expected to combine initially with gypsum and lime to form a solid solution of the high sulphate sulphoaluminate and sulphoferrite. As with C_3A , this phase converts later, when the sulphate is exhausted into a low-sulphate aluminoferrite solid solution and/or a more complex solid-solution phase in which sulphate ion is replaced by hydroxyl ion. The only exception to this behavior occurs in cements of low C_3A content.

Some of the Al_2O_3 , Fe_2O_3 and SO_3 is taken up initially in the C-S-H gel but only the alumina seems to be retained in significant quantity indefinitely. Some Al_2O_3 as well as Fe_2O_3 and SiO_2 enters into a hydrogarnet phase. The rest of the alumina and ferric oxide from the C_3A and

C_4AF , together with the SO_3 , may be expected ultimately to be present in the hexagonal-plate solid solution.

The initial hydration products of C_3S and β - C_2S have a composition close to $C_3S.aq.$ and $C_2S.aq.$ but within a matter of hours these change to a C-S-H gel with a $CaO:SiO_2$ ratio to the region of 1.5. The final composition of this gel varies from about 1.5 to 1.8 with the cement, the water-cement ratio and the temperature. It is also influenced by the amount of other oxides remaining in the gel.

The hydration products of cement are all compounds of relatively low solubility, were it not so, mortars and concretes would not remain stable in contact with water, but would rapidly suffer attack.

A schematic representation of the reactions during the hydration of Portland cement at ordinary temperatures is set out below in Figure 4.1.

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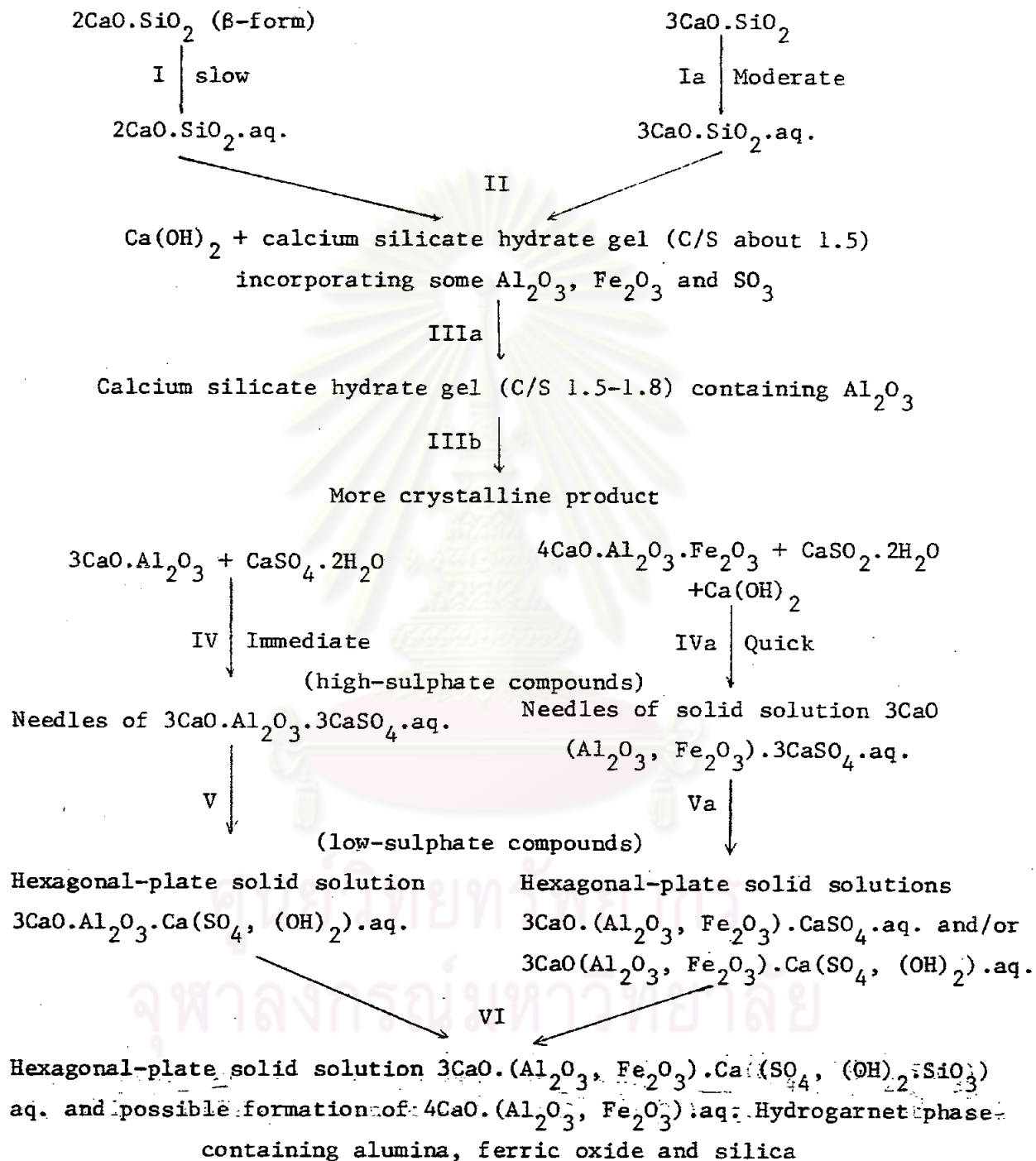


Fig. 4.1 Hydration of Portland Cement

4.3 Theories of Setting and Hardening in modern views

There is still no general agreement about the details of the processes which cause setting and hardening, but the following summary would probably be accepted by the majority of investigators at the present time. It is given in terms of Portland Cement hydrated at ordinary temperatures. The mechanism²⁷ is as follows.

The initial result of mixing the cement with water is to produce a dispersion; the water/cement ratio needed to produce a paste is such that the grains of cement are not close packed (Fig. 4.2 a). Reaction with water quickly produces a surface layer of hydration products on each grain. These occupy space partly at the expense of the grains, and partly at that of the liquid (Fig. 4.2 b). The particles of the hydration products at this stage are largely of colloidal dimensions (10-1000 \AA), but some larger crystals, Ca(OH) and Al^{+++} , Fe^{+++} and So_4^{--} containing phases, may also be formed. Thus when an unhydrated cement core is surrounded by hydration products the water can only reach it by diffusion through this surface film. The solution quickly becomes saturated with Ca^{++} , OH^- , SO_4^{--} and alkali cations. With further reaction, the coatings of hydration products extend and begin to meet each other, so that a gel in the classical sense is formed in the space between the grains (Fig. 4.2 c). This is the stage of setting. While still in a plastic condition the cement paste shrinks slightly because there is a contraction in volume of the system (cement + water) on hydration. Once the mass becomes rigid a small expansion sets in for the gel mass deposits around the cement grains and cause them to swell and to exert an outward pressure. The quantity of the gel mass progressively increases with time and it spreads

into the inter-granular spaces.

With still further reaction, the particles between the clinker grains become increasingly densely packed, until the material can equally well be regarded as a mass of particles in contact with each other. Differentiation of the gel also occurs in that it becomes more densely packed in some regions and less so in others, so that pores are formed. Crystalline particles ($>1\mu$) are disseminated through the gel and also form in the pores by recrystallization (Fig. 4.2 d). Where they are in the gel, they appear to have either no effect at all on the latter's structure, or at the most to produce only a local ordering either of the internal structure of the individual particles or of the way in which these are arranged. On drying the set cement it undergoes an irreversible contraction and reduction in water content as the gel changes into its more stable form. On very prolonged ageing, a further slow change may occur by crystal growth. There is, however, a reduction in the surface area with ageing indicating that irreversible changes towards a more stable state are occurring.

As stated earlier, the forces which bind the colloidal particles together in the gel are not definitely known. Perhaps the most important are hydrogen bonds, van der Waals forces, and ionic attractions of various kinds, caused by the occurrence of unbalanced electrical charges. Si-O-Si bonds may also be formed.

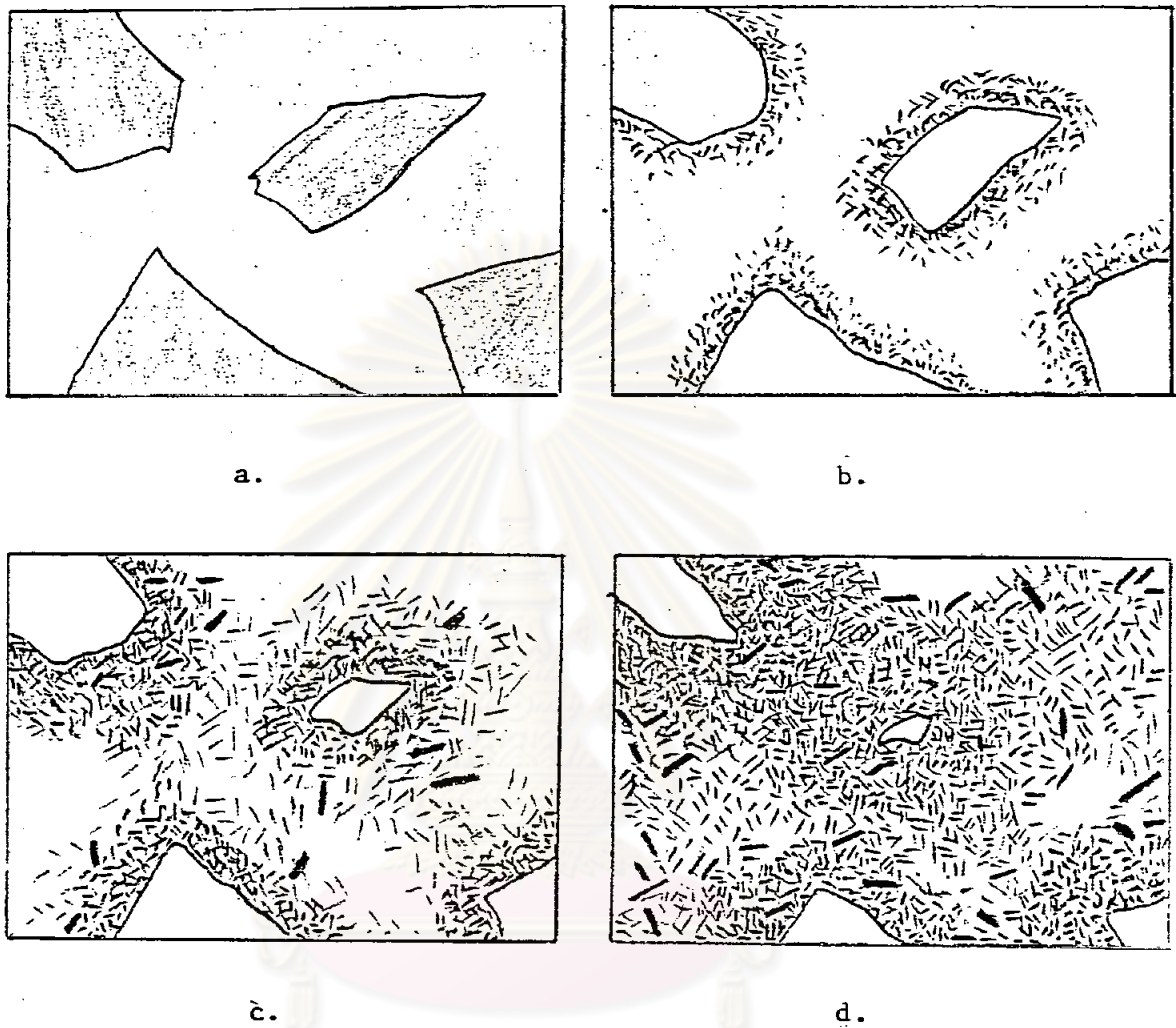


Fig. 4.2 Four stages in the setting and hardening of Portland cement: simplified diagrammatic representation of the possible sequence of changes.

- Dispersion of unreacted clinker grains in water
- After a few minutes: hydration products eat into a grow out from the surface of each grain
- After a few hours: the coatings of different clinker grains have begun to join up, the gel thus becoming continuous (setting)
- After a few days: further development of the gel has occurred (hardening)



- Fig. 4.3 Portland Cement immediately after mixing with Water (x 70)



- Fig. 4.4 Portland Cement 24 hours after mixing with Water (x 70)