

Chapter 2 Hydration, setting and hardening of Portland cement

2.1 Introduction

In chemical terms, hydration is a reaction of an anhydrous compound with water, yielding a new compound named a hydrate. In cement chemistry, hydration is understood to be the reaction of a non-hydrated cement or one of its components with water, associated with both chemical and physico-mechanical changes of the system, particularly with regard to setting and hardening. The chemical reactions taking place during hydration are generally more complex than simple conversion of anhydrous compounds into the corresponding hydrates (Hewlett, 1998a; Taylor, 1997).

A mixture of cement and water in such proportions that setting and hardening occur is called a paste. The mutual ratio of water and cement in the mix (the water/cement (w/c) ratio) refers to proportions by mass, which for a paste is typically 0.3-0.6. This ratio affects the rheology of the produced suspension, the progress of hydration and the properties of the hydrated material. Setting of cement is stiffening without a significant development of compressive strength, and typically occurs within a few hours. Hardening follows the setting of the cement paste, and means the development of compressive strength, which is normally a slower process. Curing means storage under conditions such that hydration occurs, which in laboratory studies include storage in moist air initially and then in water after the first 24 hours, or storage in air of 100% humidity and, less favourable, storage in a sealed container (Hewlett, 1998a; Taylor, 1997).

Because Portland cement is a multi-component system, its hydration is a complex process consisting of a series of individual chemical reactions that take place both simultaneously and successively. The process is initiated spontaneously upon contact of the binder with water, and is associated with liberation of heat.

The progress of hydration and its kinetics are influenced by a number of factors, of which some are the phase composition of the cement and presence of foreign ions within the crystal lattices of the individual clinker phases, the fineness of the cement, the water-cement ratio, the curing temperature, and the presence of chemical admixtures and additives (Hewlett, 1998a).

2.2 Hydration of the individual phases in Portland cement

2.2.1 Tricalcium silicate

Tricalcium silicate, $3\text{CaO}\cdot\text{SiO}_2$ (abbreviated as C_3S), is the main component of Portland cement, and is the phase that primarily controls the early setting and hardening. The products of hydration of this phase at ambient temperatures are an ill-defined amorphous calcium silicate hydrate phase called the C-S-H phase and crystalline calcium hydroxide, also referred to as portlandite, $\text{Ca}(\text{OH})_2$ (abbreviated as CH). The hydration reaction may be shown as



or abbreviated as



where m and n are not necessarily integers (Bye, 1999; Hewlett, 1998a).

2.2.2 Dicalcium silicate

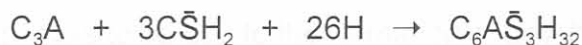
The β -modification of dicalcium silicate, $2\text{CaO}\cdot\text{SiO}_2$ (abbreviation C_2S) is the most regular constituent of C_2S in Portland cement. Similarly to C_3S , its hydration products are also C-S-H and calcium hydroxide. The amount of calcium hydroxide being produced during the hydration of $\beta\text{-C}_2\text{S}$ is about a fifth of that produced in the hydration of C_3S , and the rate of hydration of $\beta\text{-C}_2\text{S}$ is much slower than that of C_3S (Bye, 1999).

2.2.3 Tricalcium aluminate

The reaction of tricalcium aluminate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (abbreviation C_3A), with water in suspensions at ordinary temperatures gives C_2AH_8 and C_4AH_{19} , which are subsequently converted into C_3AH_6 (Taylor, 1997). The conversion to C_3AH_6 is accelerated with increasing temperature and also depends on the water/solid ratio, the grain size of C_3A and the presence or absence of CO_2 .

In the presence of calcium hydroxide, the rate of reaction slows down and only C_4AH_{19} is formed as primary product (Hewlett, 1998a). It again converts to C_3AH_6 as the hydration progresses.

In the presence of calcium sulphate the amount of C_3A in the initial stage of hydration is noticeably reduced when compared to that consumed in the absence of CaSO_4 . Ettringite (trisulphate), $\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$ is formed as the main product of hydration (Hewlett, 1998a, Taylor, 1997):



Ettringite belongs to the broad group of Aft phases with the general formula $[\text{Ca}_3(\text{Al}, \text{Fe})(\text{OH})_6]\text{X}_3\cdot x\text{H}_2\text{O}$, where X represents a formula unit of a doubly charged anion.

After a rapid initial reaction, the hydration rate is slowed down, and the length of this dormant period may vary with the amount of calcium sulphate present in the original paste. A faster hydration is initiated after all of the available gypsum has been consumed. Under these conditions, the ettringite formed initially reacts with additional amounts of C_3A , yielding calcium aluminate monosulphate hydrate (monosulphate), $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$ (Taylor, 1997):



As ettringite is gradually consumed, calcium aluminate hydrate, C_4AH_{19} , also starts to form. In a paste hydration at ambient temperature, a nearly complete hydration of C_3A is attained within several months. The origin of the dormant period, which is characterised by a discretely reduced reaction rate, is not obvious and many theories exist to explain it.

The most widely accepted theory assumes the build-up of a layer of ettringite at the surface of C_3A which acts as a barrier responsible for the slowing down of the reaction. Ettringite is formed in a through solution reaction and precipitates at the surface of C_3A due to the limited solubility of C_3A in the presence of sulphates.

The termination of the dormant period appears to be due to a breakdown of the protective layer, as the added gypsum becomes consumed and ettringite is converted to monosulphate. During this solution reaction both C_3A and ettringite dissolve and monosulphate is precipitated from the liquid phase (Hewlett, 1998a).

2.2.4 Calcium aluminoferrite

The composition of calcium aluminoferrite may vary between approximately $C_2(A_{0.7}, F_{0.3})$ and $C_2(A_{0.3}, F_{0.7})$ (Hewlett, 1998a). As with C_3A , the progress of hydration is slowed in the presence of calcium hydroxide and gypsum. The retardation in the presence of gypsum and calcium hydroxide appears to be due to the formation of an Aft layer at the $C_2(A, F)$ surface.

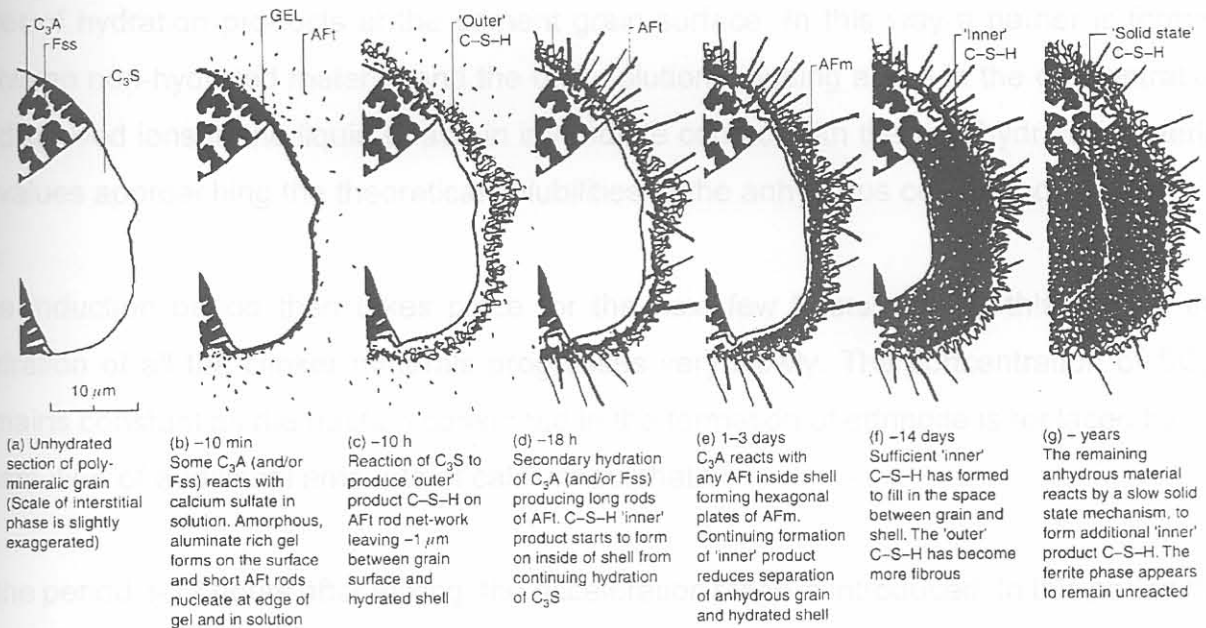
2.3 Hydration of Portland cement

Chemically, the hydration of Portland cement consists of a series of reactions between the individual clinker minerals, calcium sulphate and water, which proceed both simultaneously and successively at different rates and influence each other (Hewlett, 1998a). The participants of the process are alite (tricalcium silicate doped with foreign ions), belite (dicalcium silicate doped by foreign ions), tricalcium aluminate, calcium aluminate ferrite, free calcium oxide, alkali sulphates, calcium sulphate in the form of dihydrate, hemihydrate or anhydrite interground with clinker, and mixing water.

The progress of the process depends on the rate of dissolution of the involved phases, the rate of nucleation and crystal growth of the hydrates to be formed, and the rate of diffusion of water and dissolved ions through the hydrated material already formed. At the beginning of hydration, the process tends to be controlled mainly by the rate of dissolution of the

clinker phases and calcium sulphate. The quantity and form of calcium sulphate plays an important role in the kinetics of the hydration process. A schematic presentation of the hydration of a polymineralic grain of Portland cement is given in Figure 2.1.

Figure 2.1 Hydration of a grain of Portland cement (Bye, 1999; Taylor, 1997)



The hydration of Portland cement is characterised by several stages (Hewlett, 1998a). During the pre-induction period, which takes place in the first minutes upon contact of cement with water, a rapid dissolution of ionic species into the liquid phase and the formation of hydrate phases is initiated. Alkali sulphates present in the cement dissolve completely within seconds, contributing K^+ , Na^+ and SO_4^{2-} ions. Calcium sulphate dissolves until saturation, thus contributing Ca^{2+} and additional SO_4^{2-} ions.

Tricalcium silicate (C_3A) dissolves similarly and a layer of the C-S-H phase precipitates at the cement particle surface. As the CaO/SiO_2 ratio of the produced hydrate is lower than that of tricalcium silicate, the hydration of this phase is associated with an increase of the Ca^{2+} and OH^- concentration in the liquid phase. At the same time, silicate ions also enter

the liquid phase, although their concentration remains very low. Consequently, the setting that has been formed during the early stages. Tricalcium aluminate (C_3A) dissolves and reacts with Ca^{2+} and SO_4^{2-} ions (from gypsum) present in the liquid phase, yielding ettringite that also precipitates at the cement particle surface. The ferrite phase reacts in a very similar way as C_3A , and also yields ettringite.

The early fast hydration reaction appears to be slowed down due to the deposition of the layer of hydration products at the cement grain surface. In this way a barrier is formed between non-hydrated material and the bulk solution, causing a rise in the concentration of dissolved ions in the liquid phase in immediate contact with the non-hydrated material to values approaching the theoretical solubilities of the anhydrous compound.

The induction period then takes place for the next few hours. During this period, the hydration of all the clinker minerals progresses very slowly. The concentration of SO_4^{2-} remains constant as the fraction consumed in the formation of ettringite is replaced by the dissolution of additional amounts of calcium sulphate.

In the period 3-12 hours after mixing, the acceleration stage is introduced. In this period the progress of hydration is accelerated again and is controlled by the nucleation and growth of the hydration products. The rate of C_3S hydration accelerates and the second-stage C-S-H starts to be formed. A noticeable hydration of dicalcium silicate also takes place. Crystalline calcium hydroxide precipitates from the liquid phase and together with it the concentration of Ca^{2+} in the liquid phase gradually declines. The calcium sulphate, interground with the cement becomes completely dissolved and the concentration of SO_4^{2-} in the liquid phase starts to decline due to the formation of ettringite, as well as the adsorption of SO_4^{2-} on the surface of the formed C-S-H phase.

During the post-acceleration period, the hydration rate slows down gradually, as the amount of still non-reacted material declines as the rate of the hydration process becomes diffusion controlled. The C-S-H phase continues to be formed due to the continuing hydration of both C_3S and β - C_2S . The contribution of β - C_2S to this process increases with time with a subsequent decline in the rate at which additional calcium hydroxide is formed. After the

supply of calcium sulphate has been depleted, the concentration of SO_4^{2-} in the liquid phase declines. Consequently, the ettringite that has been formed during the early stages of hydration starts to react in a through-solution reaction with additional C_3A to yield monosulphate. After the hydration process has been completed, ageing of the hydrated material takes place (Hewlett, 1998a; Taylor, 1997).

2.4 Setting of Portland cement

Setting is a process in which a 'fresh' cement paste of freely flowing or plastic consistency is converted into a set material which has lost its unlimited deformability and crumbles under the effect of a sufficiently great external force (Hewlett, 1998a).

After mixing a Portland cement with an adequate amount of water, the cement grains are initially evenly distributed in the liquid phase. Within minutes from mixing, flocculation of the cement particles takes place, which is associated with an increase in the viscosity of the paste. Individual aggregates of cement particles are formed which entrap a fraction of the mixing water, thus making it unable to participate in the flow of the paste. This initial flocculation of cement particles is caused by opposite zeta potentials and by weak van der Waals forces.

2.5 Strength development in Portland cement

In addition to flocculation, the viscosity of the paste also increases due to a progressive hydration of the cement that results in an increase of the solid/liquid ratio. During the acceleratory stage of hydration, the amount of hydrated material increases rapidly and the volume of the liquid phase declines. Chemical bonds develop at the points of contact between the individual cement particles, which are covered with the hydrated material. As the amount of hydrated material increases, the number of contacts between particles also increases and eventually a continuous three-dimensional network of solids develops within the paste, resulting in the set of the paste. The normal setting of Portland cement appears to be the consequence of both C_3S and C_3A hydration and the formation of the C-S-H and Aft phases (Hewlett, 1998a).

To produce a cement with acceptable setting characteristics, calcium sulphate has to be added or interground with the clinker to act as a set retarder. In the presence of sufficient amounts of Ca^{2+} and SO_4^{2-} in the liquid phase, the amount of C_3A and C_4AF hydrated in the initial pre-induction period is reduced, and ettringite (AFt) is formed during the hydration.

Flash set (also referred to as quick set) occurs when the amount of gypsum added is not sufficient. This is a rapid set, with much evolution of heat. Plasticity is not regained on continued mixing and the strength development of the paste is poor. It is associated with increased early reaction of the aluminate and ferrite phases with a subsequent formation of plates of the Afm (Al_2O_3 - Fe_2O_3 -mono) phase throughout the paste, which accounts for the rapid stiffening (Taylor, 1997).

Another undesirable condition is called false set. It is also a rapid set, but there is no unusual high evolution of heat, and plasticity is regained on further mixing. The strength development is not affected noticeably. The most usual cause of false set is the presence of too much calcium sulphate in the form of hemihydrate, which is rehydrated to yield gypsum. The setting is attributable to the interlocking of gypsum crystals.

2.5 Strength development in Portland cement

The strength of cement is defined as the strength of mortar test specimens prepared, cured and tested according to a national or international testing standard, to eliminate the effect of factors other than cement quality on the obtained value.

The strength of a hardened cement paste is due to the presence of a continuous three-dimensional network of hydrate phases which can resist external stresses without being broken down. Of the three components of the hardened paste, i.e. hydrated material, non-hydrated residual cement and pores, the hydrated material is the constituent which is mainly responsible for the obtained strength. The non-hydrated material present acts as a filler and also exhibits the capacity to resist external stresses.

For a given degree of hydration, the respective clinker minerals contribute to the strength of the cement in the order $C_3A < C_4AF < C_3S < C_2S$. This indicates the existing differences in the intrinsic strengths of hydrates formed during hydration of the individual clinker phases (Hewlett, 1998a).

3.1 Impurities in phosphogypsum

The amounts of impurities in phosphogypsum depend upon the quality of the raw material used, the operating conditions of the phosphoric acid process, and the age of the plant (Brady, 1977). Oxidation of phosphogypsum from plant to plant varies due to variations in raw material, the fluctuation in the climatic conditions under which they are stored, and the fluctuating conditions of the process (1,50% concentration, 100°C temperature, acidic atmosphere) (amount of 1,50%) (Gardall et al, 1977).

To be able to use phosphogypsum in the construction industry, it is necessary to know the impurities contained in the phosphogypsum. The impurities are divided into two groups, (1) free phosphoric acid, which was used in the production of phosphoric acid and (2) disodium phosphate (Brady, 1977). The impurities in the crystal lattice of gypsum (Olmer and Linder, 1978) (Brady, 1977) are neutralized, the impurities contained in phosphogypsum exist in acidic form (Brady, 1977).

3.2 The influence of phosphogypsum impurities on the mechanical strength and hydration of Portland cement

Tabikh and Miller (1977) stated that the chemical process employed in the production of phosphogypsum yields a product of widely varying impurity concentrations. Percentage amounts of impurities interfere in an unpredictable way with the hydration of Portland cement.