

CHAPTER 2.

THEORETICAL APPROACH

Cements are defined as adhesive substances capable of uniting fragments or masses of solid matter to a compact whole⁽³⁾. The oldest cementing material was simply mud, clay mixed with straw to bind bricks together. This is found in ancient Egyptian buildings. But these buildings, which used clay, have no resistance to water. The calcareous materials (cements based on lime compounds) were used as cements to bind bricks. These materials were prepared by calcining impure gypsum and lime and are still nonhydraulic, because hardening will not take place under water.

Hydraulic limes were produced by the Greeks and the Romans. These cements were prepared by calcining limestones containing clay-like impurities, yielding a mortar which had more strength and was water-resistant.

Later in 1756, John Smeaton built the Eddystone Lighthouse which used hydraulic lime mixed with pozzolan imported from Italy. These buildings stood for 126 years before being replaced by modern structures.

The development of hydraulic cement was discovered and patented by James Parker in England in 1796. This cement was produced by calcining modules of impure limestone containing clay. In 1813, L.J. Vicat investigated hydraulic lime by calcining an intimate mixture of limestone(chalk) and clay, ground together in a wet mill. James Frost introduced the same approach in England in 1822.

In 1824, Joseph Aspdin took out a patent on "portland cement". He used a hard limestone as is used for repairing roads, crushed and calcined it in a furnace. But the temperature of his calcine was low, and the product must have been of poor quality. Isaac Charles Johnson in 1845, used a higher temperature of firing than Aspdin. This made the mixture burn at real clinker temperature. The name portland cement was given to the product, the color of which resembles that of cement after setting it to Portland stone.

2.1 CEMENT COMPOSITION

The compound presence of cements is formed by the chemical reaction during the burning of lime, silica, alumina and ferric oxide compounds that come from raw materials. Portland cement is composed of over 90 percent of lime, alumina and silica. The effects of minor compounds' components on the portland cement are also considered. The temperature that produces portland cement is below the complete fusion temperature. This temperature makes only a minor proportion of the reacting mixture melt and clinker is formed.

2.1.1 BASIC OXIDE COMPOUND

Silicon Dioxide, SiO₂

Silica is the main component of sand and pozzolans as a constituent of mortar. It is derived from the clay and shale used as raw materials. Pure crystalline occurs in nature as Quartz which consists of hexagonal crystals belonging to the trigonal system. The specific gravity is 2.651 and hardness 7.

Quartz is a very inert substance at ordinary temperature. But at high temperatures, it will react with bases. This is the reason why sand will not react with lime or cement in mortars. But quartz will react with lime in the presence of water if heated under high pressure. The combination of silica with water gives rise to the silica acid gel.

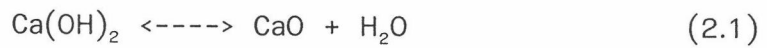
Calcium Oxide, CaO

Lime is an essential component of the cements. It is derived from the decomposition of calcium carbonate, CaCO₃. The color of pure lime is white, amorphous and it is a friable material. The specific gravity of lime varies from 3.08–3.30.

The melting point of lime is 2,614°C. The crystallizes are colorless or pale yellow. If it is placed in water, it dissolves very slowly at the surface. The hydration is gradual and there is no temperature rise. Lime prepared in room temperature is loose and porous.

Calcium Hydroxide, Ca(OH)_2

Calcium hydroxide is the product of the hydration reaction of lime and water. Pure calcium hydroxide will decompose into lime and water vapour at 400°C as shown in equation 2.1.



It is not found in cement clinker after burning. It is produced during the grinding of cements while adding gypsum. If mixed with water and crystallized slowly as a hydration reaction of cement, it will form large hexagonal plate crystals. Calcium hydroxide can be reacted with carbon dioxide to form calcium carbonate. This reaction causes deterioration of concrete in the presence of moisture.

Aluminium Oxide, Al_2O_3

Alumina occurs in nature as corundum. The melting point is $2,045^\circ\text{C}$. It does not seem to exist as a pure oxide but is formed in compounds. Combined alumina is an important constituent in cements. It also occurs freely in a hydrated form gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and bauxite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) in nature. Hydrated alumina will not be formed during hydration of portland cement. Normally hydrated alumina will occur in the setting of high alumina cement.

Ferric Oxide, Fe_2O_3

Iron oxides are derived from clay or shale. But in high alumina cement it is derived from bauxite. Ferrous oxide occurs in small amounts of about 0-4 percent in portland cement. Ferric oxide acts as an acid radical in cements. The melting point of pure ferric oxide is unknown. It dissociates before reaching melting point. There are 3 forms of hydrated ferric oxide. The alpha, beta and gamma forms. The alpha and gamma ferric oxides occur in nature but beta form has not been found in nature.

Magnesium Oxide, MgO

Magnesia is only present in small amounts in portland cement. Magnesia can be derived from magnesium carbonate original present in limestone in the form of

dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$). Pure magnesium oxide possesses hydraulic properties. The hydroxide $\text{Mg}(\text{OH})_2$ will occur when combined with water. Magnesia is soluble to some extent in lime at a high temperature. The melting point of MgO is $2,852^\circ\text{C}$. It shows perfect cubic cleavage. It can form naturally in the form of periclase. Magnesium hydroxide can decompose into magnesia and water at low temperatures of about $350\text{--}380^\circ\text{C}$.

2.1.2 COMBINATION OF BASIC OXIDE COMPOUND

Calcium Silicate

When lime and silica are heated together, they will form 4 distinct compounds, the metasilicate $\text{CaO} \cdot \text{SiO}_2$, the compound $3\text{CaO} \cdot 2\text{SiO}_2$, the orthosilicate $2\text{CaO} \cdot \text{SiO}_2$ and the compound $3\text{CaO} \cdot \text{SiO}_2$. The calcium orthosilicate is present in cements and slags. It melts at $2,130^\circ\text{C}$ and exists in four well established forms; γ (Orthorhombic), β (Monoclinic), α' (Orthorhombic) and α (Hexagonal). The tricalcium silicate in portland cement is usually in the monoclinic form but it can sometimes be found in trigonal and triclinic forms. It is not pure C_3S but contains various other oxides in solid solution and has some influence in strength.

Calcium Aluminate

Four stable compounds occur in the system of $\text{CaO}-\text{Al}_2\text{O}_3$ namely, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$. All these compounds melt incongruently and have primary crystallisation fields in the binary system. Tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is unstable at its melting point and melts at a temperature of $1,539^\circ\text{C}$. This melting causes dissociation into CaO and liquid compositions of calcium oxide and aluminium oxide. In the portland cement, tricalcium aluminate occurs in equant grains and shows a crystalline outline. It belongs to the cubic or isometric system with a density of 3.04.

Calcium Aluminium Ferrites

The systems of calcium-aluminium-ferrites occur in portland cement as brownmillerite. The definite composition of brownmillerite is $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and it

melts at 1,415°C. The ferrite phase in portland cement can vary in composition from C_6AF_2 to C_6A_2F . However, the average composition is approximately C_4AF .

Calcium Aluminium Silicate

This three-compound system forms some 90 percent of portland cement and over 80 percent of high alumina cement. There are many forms of products in this system depending on the temperature and the amount of each compound. The ternary compound $2CaO \cdot Al_2O_3 \cdot SiO_2$ (Gehlenite) melts congruently at 1,584°C. The crystalline substance has clear grains and belongs to the tetragonal system with a specific gravity of 3.038. This compound can not be found in portland cement but it is a constituent of some high alumina cement.

2.1.3 HYDRATION REACTION OF THE CEMENT COMPOUNDS

All compounds of portland cement are anhydrous. When mixed with water they are decompose and form hydrated compounds. The mechanisms of hydration can be divided into 2 mechanisms;

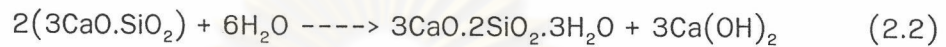
- The through-solution mechanism occurs by dissolving a cement compound into a solution. This mechanism produces ions and then combines to precipitate the hydrated products.
- The topochemical reaction occurs more slowly and takes place on the surface of cement grains without the cement compounds going into solution.

2.1.3.1 CALCIUM SILICATE

The products of hydration reaction of tri or di calcium silicate with water are calcium hydroxide and calcium silicate hydrate gel, CSH gel. The calcium silicate hydrate gels which are produced during hydration reaction change during the period of hydration and also vary with the water-solid ratio of the mixture. The CSH gel are composed of CSH-(I) and CSH-(II). The CSH-(I) consists of poorly crystallised foils or platelets with a tobermorite-like structure and has a $CaO:SiO_2$ ratio of 0.8-1.5. The CSH-(II) consists of fibrous structure. The molar ratio of $CaO:SiO_2$ is 1.5-2.0.

A. TRICALCIUM SILICATE, C₃S

When ground C₃S is mixed with water, hydration reaction occurs rapidly and both lime and silica pass into solution. The concentration of lime in solution increases steadily while silica rapidly decreases. Calcium hydroxide becomes nearly amorphous of hydrated calcium silicate. Complete hydration can only be obtained within 1 year or more. This reaction occurs with time and the approximate complete hydration reaction is shown in equation 2.2.



For a complete hydration of C₃S compound, 456 g. of C₃S reacts with 108 g. of water yielding 342 g. of calcium silicate hydrate and 222 g. of calcium hydroxide. The hydration reaction is more correctly represented in a generalised form in equation 2.3

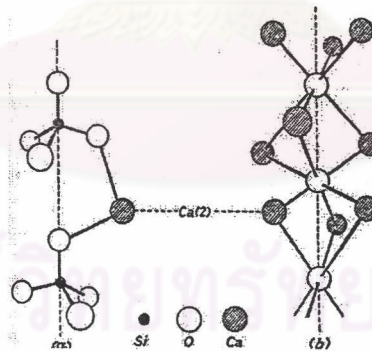
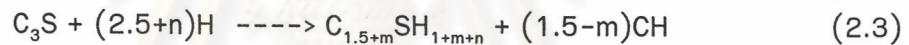


Fig. 2.1 Structure of tricalcium silicate.

The rate of hydration reaction of C₃S when mixed with water is rapid (Stage 1). This reduces within 15 minutes. The following period is a dormant period (Stage 2). At the end of the dormant period (2-4 hrs.), cement starts initial set. The silicate continues to hydrate rapidly in the acceleration period (Stage 3). Maximum heat evolution occurs in this stage. At this time, final set has been passed and cement starts hardening. After this period (4-8 hrs.), the rate of reaction slows down again (Stage 4).

until reaching a steady state (Stage 5) within 12-24 hrs. The rate of hydration of tricalcium aluminate is shown in figure 2.2.

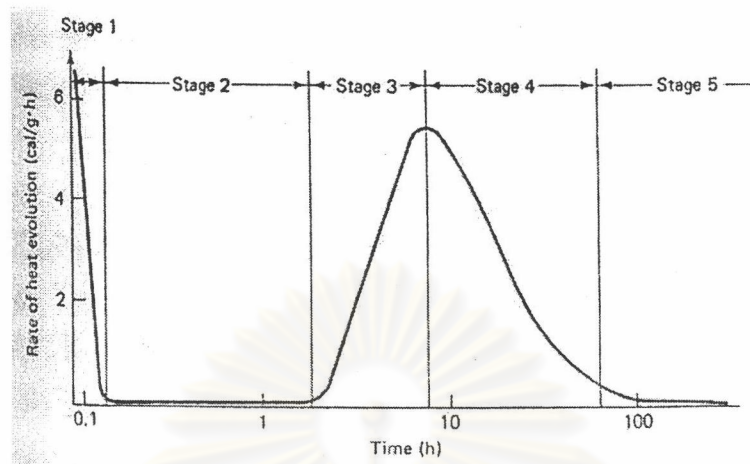


Fig. 2.2 Rate of hydration of tricalcium silicate.

The amount of C_3S in a typical ordinary portland cement type I is 45-55% (~50%). Since C_3S produces high heat of hydration and early strength, the amount of C_3S in high early strength cement type III is 50-65% (~60%). In low heat of hydration portland cement type IV, the amount of C_3S must be lower between 25-35% (~25%). The amount of C_3S is 40-50% (~40%) in sulfate resistant portland cement type V.

B. DICALCIUM SILICATE, C_2S

There are four main forms of dicalcium silicate, γ , β , α' and α . The hydration reaction of C_2S is slower than the hydration of C_3S but the CSH gels are the same type as those from C_3S . Complete hydration of dicalcium silicate can be obtained by grinding with excess water in a ball mill. This reaction can be completed within 46 days. This reaction can be written as in equation 2.4.



$$344 \text{ g.} + 72 \text{ g.} \text{ ----> } 342 \text{ g.} + 74 \text{ g.}$$

This reaction occurs with time and for complete hydration, 344 g. of C_3S reacts with 72 g. of water which yields 342 g. of calcium silicate hydrate and 74 g. of calcium hydroxide.

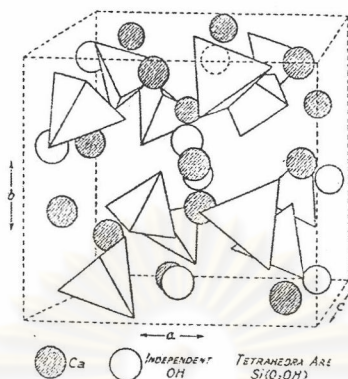
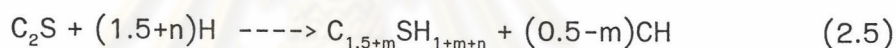


Fig. 2.3 Simplified structure of C_2S .

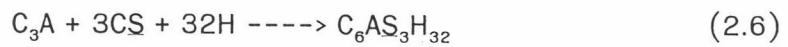
The generalised equation at any age or water is shown in equation 2.5.



The rate of hydration and strength developed is similar to C_3S but much slower because C_2S is a less reactive compound than C_3S so C_2S contributes to the later age of strength. The amount of C_2S in a typical ordinary portland cement type I is 20-30% (~25%). The amount of C_2S in high early strength cement type III is 15-25% (~15%). In low heat of hydration portland cement type IV, the amount of C_2S is approximately 50%. And the amount of C_3S is 25-35% (~30%) in sulfate resistant portland cement type V.

2.1.3.2 TRICALCIUM ALUMINATE, C_3A

The fine tricalcium aluminate reacts very rapidly with water and forms C_3AH_6 , C_4AH_{19} and C_2AH_8 which is useless for any engineering purpose. The addition of gypsum in cement slows down the reaction and forms ettringite, $C_6AS_3H_{32}$. In the presence of excess water, the formation of hexagonal plate crystals can be observed. This formation looks like needles which often form clusters radiating from a center. This crystal is formed within a few minutes and increases rapidly in size and amount. The hexagonal plate hydrates are nonstable and transform into the less soluble and more stable isometric compound $3CaO \cdot Al_2O_3 \cdot 6H_2O$. The hydration reaction is shown in equation 2.6.



Mass 268 g. + 408 g. + 576 g. ----> 1,252 g.

268 g./3.03 + 408 g./2.32 + 576 g. ----> 1,252 g./1.75

Volume 88 cm³ + 175 cm³ ----> 715 cm³

For complete hydration, 268 g. of C₃A react with 408 g. of gypsum and 18 g. of water yielding ettringite 1,252 g.

The common name of calcium sulfoaluminate hydrate (C₆AS₃H₃₂) is ettringite. Ettringite is a stable hydration product only when there is an ample supply of sulfate. If the sulfate is consumed before the C₃A has completely hydrated, ettringite will transform into another calcium sulfoaluminate hydrate containing less sulfate. The transformation reaction is shown in equation 2.7.



When monosulfate aluminate comes into contact with the new source of sulfate ions, ettringite can be formed again.

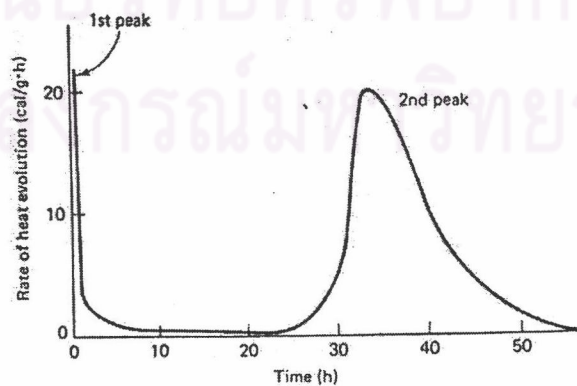
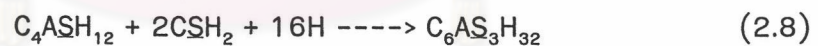


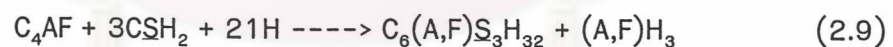
Fig. 2.4 Rate of hydration of C₃A with gypsum.

The rates of hydration of C_3A are rapid but are slowed down by the formation of ettringite creating a barrier around C_3A . This barrier is broken down during the conversion of monosulfoaluminate and C_3A starts to react rapidly again. The figure 2.3 shows rate of hydration of C_3A . The first peak is completed in 10-15 minutes but the time of the second peak depends on the amount of sulfate available.

The more gypsum there is in the mixture, the more stable ettringite remains. Conversion of monosulfoaluminate will occur in most cement within 1-2 days after gypsum has been used to form ettringite. The amount of C_3A in a typical ordinary portland cement type I is 8-12% (~12%). The amount of C_3A in high early strength cement type III is 8-14% (~10%). In low heat of hydration portland cement type IV, the amount of C_3A is approximately 5%. And the amount of C_3A is 0-4% (~4%) in sulfate resistant portland cement type V.

2.1.3.3 TETRACALCIUM ALUMINOFERRITE, C_4AF

The rate of hydration reaction of calcium aluminoferrites with water is rapid but will slow down with additional gypsum. The rate of hydration also depends on the amount of alumina in aluminoferrite. When the amount of alumina in mixtures is high, the reaction takes place rapidly but less than the hydration of C_3A . The hexagonal plate crystals are rapidly formed when mixed with water. The calcium hydroxide is not precipitated during the hydration of C_4AF .



In the presence of excess lime in water, the reaction of C_4AF is less rapid and different. The hexagonal plate phase form is a solid solution of the tetracalcium compounds. This is unstable and transformation to the latter occurs more rapidly with an increase in temperature and some calcium hydroxide.

The amount of C_4AF in a typical ordinary portland cement type I is 6-10% (~8%). The amount of C_4AF in high early strength cement type III is 6-10% (~8%). In the low heat of hydration portland cement type IV, the amount of C_4AF is approximately 12%. And the amount of C_4AF is 10-20% (approximately 10%) in sulfate resistant portland cement type V.

2.1.4 PRODUCTS OF HYDRATION REACTION

2.1.4.1 CALCIUM SILICATE HYDRATE, CSH

Many different hydrated calcium silicates occur in nature but most of them are rare. The precise composition of these compounds is uncertain. This is because of the difficulty in differentiating between combined and free lime and silica as well as distinguishing adsorbed water from water of constituent. Almost all calcium silicate hydrates are prepared under a high temperature and pressure. Only compound C_2SH (CSH(I)) and C_2SH_2 (CSH(II)) are obtained at ordinary temperature.

The crystalline of hydrated calcium silicate is produced by the action of water at an ordinary temperature on the anhydrous calcium silicates or by the action of lime on silica gel. It is convenient to represent the CSH by plotting the $CaO:SiO_2$ ratio in the solid phase against the CaO concentration of the solution.

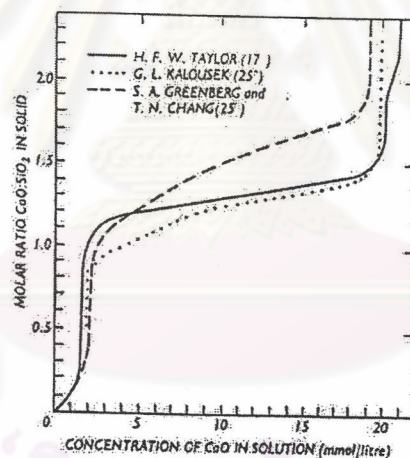


Fig. 2.5 Equilibrium between hydrous calcium silicates and solution.

From figure 2.5, the solid product with $CaO:SiO_2$ ratios varying from 1.0–1.5 showed no significant change in the pattern, indicating that the basic structure remained the same. This hydrate composition varies from $CaO.SiO_2$ aq. to $3CaO.2SiO_2$ aq. This hydrate was called calcium silicate hydrate I (CSH(I)).

The sharp rise in figure 2.3 in the lime:silica ratio of the solid phase at lime concentration near saturation could be attributed to an invariant point between CSH(I)

and $\text{Ca}(\text{OH})_2$. This hydrate was called dicalcium silicate hydrate or calcium silicate hydrate II, (CSH(II)).

The water content of the calcium silicate hydrates formed at room temperature is also difficult to define. They have a very large specific surface with water adsorption which cannot completely be separated from water of constituent. The additional molecules of water can enter between the layers of CSH and increase their spacing. The CSH I and CSH II hydrates are apparently both very closely related to the natural mineral tobermorite. The poorly crystalline or nearly amorphous calcium silicate hydrates formed in portland cement pastes at ordinary temperatures are more indefinite natural than CSH I and CSH II because they are comprised of differing phase and compositions depending on the degree of hydration, temperature and water to cement ratio.

2.1.4.2 CALCIUM HYDROXIDE, $\text{Ca}(\text{OH})_2$

Calcium hydroxide crystallizes in a hexagonal formation as plates or short hexagonal prisms. Its density is 2.3. The solubility of calcium hydroxide in water decreases with a rise in temperature.

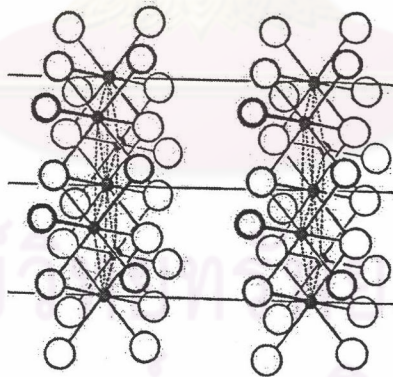


Fig. 2.6 Calcium hydroxide crystal.

Large circle of OH and small black circle of $\text{Ca}^{(2+)}$.

The small particle size gives apparently higher solubilities. A saturated solution of calcium hydroxide assigns a pH of 12.45 at 25°C and 1.14 g CaO per litre. The solubility of calcium hydroxide is much reduced in the presence of alkali hydroxides. The crystal of calcium hydroxide is shown in figure 2.6.

2.1.4.3 CALCIUM SULPHOALUMINATE (ETTRINGITE), $C_6A_3H_{32}$

The action of calcium sulphate on calcium aluminate solutions produces both high and low forms of calcium sulphoaluminate hydrate. This compound was observed in 1890 by Candlot. It occurs naturally as the mineral ettringite. The density of high sulphate form is 1.73 at 25°C and the low sulphate form is 1.99 at 20°C.

The high sulphate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$) form can be prepared by slowly adding a saturated lime solution with aluminium sulphate and calcium sulphate as shown in equation 2.10.

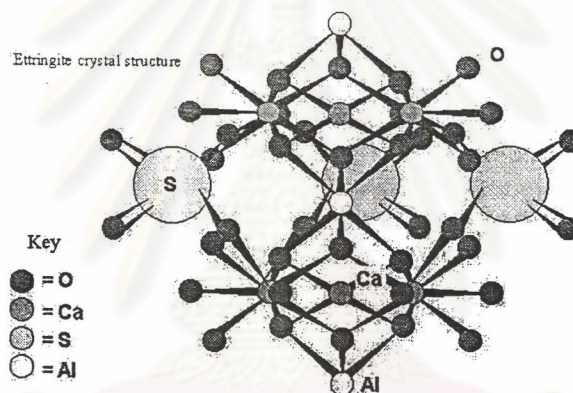
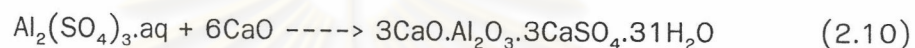
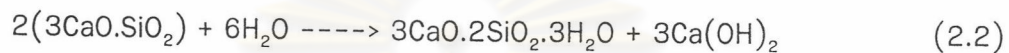


Fig. 2.7 Crystal structure of ettringite⁽³⁰⁾.

It is difficult to obtain purity with the low sulphate form, $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$, since it enters into solid solution with C_4AH_{13} . It can be prepared at 25°C by treating a monocalcium aluminate solution with lime-calcium sulphate solution. The crystal is formed as hexagonal plates and needles with a pseudo hexagonal uniaxial crystal system.

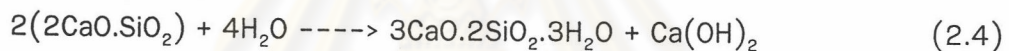
2.2 SHRINKAGE THEORETICAL APPROACH

The dimension of cement pastes will not remain constant due to the loss of adsorbed water from hydration products, mainly calcium silicate hydrate (CSH). C_3S and C_2S are the main chemical constituents that produce calcium silicate hydrate. In ordinary portland cement 100 g. (32 cm^3), the amount of tricalcium silicate and dicalcium silicate is approximately 52 g. and 25 g. respectively. The specific gravity of C_3S is 3.5, CSH is 2.44 and $\text{Ca}(\text{OH})_2$ is 2.23 then the volume of hydrated portland cement paste can be calculated from stoichiometric ratio as shown in equation 2.2.



$$\text{Mass} \quad 52 \text{ g.} + 12.3 \text{ g.} \text{ ----> } 39 \text{ g.} + 25.4 \text{ g.}$$

$$\text{Volume} \quad 14.9 \text{ cm}^3 \quad \text{---->} \quad 16 \text{ cm}^3 + 11.4 \text{ cm}^3$$



$$\text{Mass} \quad 25 \text{ g.} + 5.3 \text{ g.} \text{ ----> } 24.9 \text{ g.} + 5.4 \text{ g.}$$

$$\text{Volume} \quad 7.6 \text{ cm}^3 \quad \text{---->} \quad 10.2 \text{ cm}^3 + 2.4 \text{ cm}^3$$

From equations 2.2 and 2.4, the volume of dicalcium silicate and tricalcium silicate $14.9+7.6= 22.5 \text{ cm}^3$ will react with water 17.6 cm^3 producing CSH 26.2 cm^3 and calcium hydroxide 13.8 cm^3 . This calculation shows that 100 g. (22.5 cm^3) of anhydrous cement will produce 40 cm^3 of CSH and calcium hydroxide, that is 1.77 times that of anhydrous cement.

It can be assumed that cement is hydrate in normal conditions with $w/c = 0.32$, temperature at $28-30^\circ\text{C}$ and 80% RH. From Mehta⁽¹²⁾, the volume of pore in CSH is 0.28 times that of the total volume of CSH in cement paste. Then the pore volume that can contain interlayer water, W_i , in CSH is $0.28 \times (16+10.2) = 7.4 \text{ cm}^3$. This interlayer water can be removed from the CSH pastes causes shrinkage of cement pastes.

Loss of adsorbed water and capillary water also causes shrinkage. The volume of adsorbed water^(12, 13, 21) can be approximately calculated from equation 2.11.

$$W_a = 18-23\% \times M_c \quad (2.11)$$

In this equation, W_a is the volume of adsorbed water (cm^3) and M_c is the initial weight of cement (g.). Then the volume of adsorbed water is $0.23 \times 100 \text{ g.} = 23 \text{ cm}^3$.

The volume of capillary water^(12, 13, 21) can be approximately calculated from equation 2.12.

$$W_c = (w/c - 0.36) \times M_c \quad (2.12)$$

In this equation, W_c is the volume of capillary (cm^3), w/c is the water to cement ratio and M_c is the initial weight of cement (g.). If the water to cement ratio is 0.32, then the volume of capillary water is $(0.32 - 0.36) \times 100 = -4 \text{ cm}^3$. This shows that there is no water in the capillary pores then 0 cm^3 should be used. The total volume of water that can be removed from paste causing shrinkage is $7.4 + 23 + 0 = 30.4 \text{ cm}^3$.

BEHAVIOR OF SHRINKAGE

Drying shrinkage is generally reserved for hardened concrete while plastic shrinkage is used for fresh concrete.

PLASTIC SHRINKAGE

When water is removed from the paste by exterior influences, a complex series of menisci are formed. It makes negative capillary pressures which causes the volume of the paste to shrink. Capillary pressure continues to rise within the paste until a critical breakthrough pressure is reached. The breakthrough pressure is the stage where water is no longer dispersed through the paste and rearranges to form discrete zones of water with voids. After breakthrough pressure, a little plastic shrinkage will occur. The plastic shrinkage can be controlled by keeping the concrete surface wet until the surface has been finished or cured.

DRYING SHRINKAGE

Drying shrinkage can be categorized into reversible shrinkage, which is the shrinkage that is reproducible in a wet-dry process and irreversible shrinkage, which is the shrinkage on first drying that cannot be reproduced in wet-dry cycles. The drying shrinkage of cement paste that occurs on the first drying is irreversible. The volume expansions that occur on rewetting and the volume occurring in later drying are smaller. The factors affecting shrinkage are porosity, age, curing temperature, cement composition, moisture content, admixtures and aggregate.

Reversible shrinkage

The net linear shrinkage is a function of internal pressures developed by capillary stress, disjoining effects and changes in surface free energy.

A. Capillary Stress

Hydrostatic tension is only developed when a meniscus is formed in a capillary, the stress being given by

$$P_{cap} = 2\gamma / r \quad (2.13)$$

In this equation P_{cap} is capillary force, γ is the surface tension of water and r is the radius of the meniscus. The value of r is determined by the relative humidity. As water decreases in the capillaries, the meniscus curvature increases and the surface tension forces produce a tension in the water while remains in capillary. This liquid tension must be balanced by an equivalent compressive stress in the solid, producing shrinkage deformation.

B. Disjoining Pressure (Swelling Pressure)

The thickness of CSH which is increased by the water is adsorbed on the surface of CSH. The van der Waals forces attract adjacent particles and bring adjacent surfaces into close contact. Adsorption of water on CSH surfaces creates a disjoining pressure. This effect forces the solid surface of the CSH gel particles apart. A swelling

pressure develops which is related to the vapour pressures of the water inside gel by the Katz equation.

C. Surface Tension

The change in surface energy causes shrinkage at low RH. Since liquid drop under hydrostatic pressure by virtue of its surface tension is bound by a meniscus, pressure will occur and can be expressed in equation 2.14.

$$P_{sfe} = 2\gamma S / 3 \quad (2.14)$$

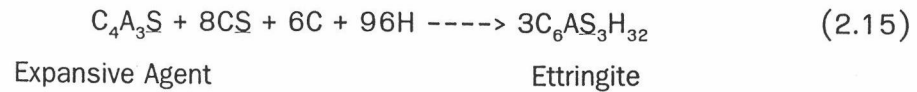
In this equation γ is the surface energy and S is the specific surface area of the solid. Since CSH has a large specific surface (S), then P_{sfe} can be large, causing compression in the solid.

Irreversible shrinkage

The irreversible shrinkage can be explained by changes in the distribution of pores within the paste. On first drying, permeability of paste increases and a continuous network of capillaries is formed. The development of capillary stress is much reduced and stresses occur. However, the irreversibility of paste can be the result of the following changes; changes in pore size distribution, changes in bonding between CSH particle and changes in the distribution of water within CSH.

2.3 EXPANSION THEORETICAL APPROACH

The expansion of paste is associated with the formation of calcium sulfoaluminate hydrate, that is ettringite. Many theories try to explain the formation mechanism of ettringite. Expansion theories can be divided into two major ones: the Crystal Growth Theory and the Swelling Theory. The hydration reaction producing ettringite from stoichiometric reaction can be shown in equation 2.15.



Mass 604 g. + 1,088 g. + 336 g. + 1,728 g. ----> 3,756 g.

Volume 13 cm³ + 22 cm³ + 5 cm³ + 80 cm³ ---- > 100 cm³

As the specific gravity of calcium sulphoaluminate is 2.20, calcium sulfate 2.32, calcium oxide 3.32 and ettringite 1.75 so in the equation 2.17, the volume 274 cm³ of calcium sulphoaluminate will react with 468 cm³ of calcium sulphate, 101 cm³ of calcium oxide and 1,728 cm³ of water producing 2,146 cm³ of ettringite. This calculation shows that 302 cm³ (604 g.) of calcium sulphoaluminate will produce 2,146 cm³ (3,756 g.) of hydration products or if 2,146 cm³ of ettringite is required, there should be 274 cm³ of expansive agent in the original mixture.

Crystal Growth Theory (Expansion Model)

The expansion is caused by the growth of ettringite crystals, which are formed on the surface of the expansive particles or in the solution. Hence, the expansive force is caused by crystallization pressure. As soon as the reaction starts, the surfaces of expansive particles (C₄A₃S) are immediately covered by ettringite. This reaction is called a topochemically reaction⁽⁷⁾. On further hydration, ettringite increases the layer thickness of the particles. The expansion caused by the thickness of the layer exceeds the surrounding solution thickness. It pushes other particles apart, hence causing overall expansion. Expansion will continue until the expansive particles or dissolved sulfate depletes. The expansion model⁽¹⁷⁾ divides the fresh expansive cement into three sub systems: the solution, the matrix and the expansive particles.

- The solution includes water, dissolved sulfates, lime and other impurities.
- The matrix includes the unhydrated calcium silicate particle, (C₃S and C₂S), surrounded by the solution. The matrix is the main strength producing system.
- The expansive particles consist of spherical cement particles, with each particle surrounded uniformly by a film of solution which is of the same thickness for each particle but different in diameter.

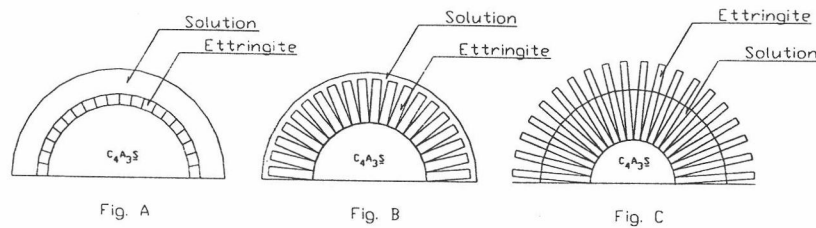


Fig. 2.8 Expansion of ettringite.

The spherical C_4A_3S particles can be assumed to have equal diameters. The reaction between C_4A_3S particles and solution produces ettringite. The spherical C_4A_3S particles are covered uniformly with ettringite crystals. The length of crystals will increase but their number and thickness will remain the same.

This process will continue as long as the necessary reactants are available in stoichiometric quantities. Expansion starts when the length of crystals becomes larger than the solution film thickness, and the crystals begin to exert pressure against the surrounding matrix.

Swelling Theory

The expansion is produced by a swelling of ettringite. Expansion of ettringite is caused by a through solution mechanism. This causes ettringite crystals to be gel like and colloidal in size.

The ettringite particles, having a large specific surface area and water molecules, can be adsorbed through the surface particles. The water adsorption will generate strong swelling pressures leading to an overall expansion of system without any change in the crystal lattice of ettringite. Ettringite with finer particles expands more than coarse ettringite⁽¹⁷⁾ because it has a large specific surface area and can adsorb more water. The classification of ettringite as “gel like” remains a subject of controversy between the theories of expansion, namely crystallization and the swelling theory.

2.4 SHRINKAGE COMPENSATION

Shrinkage of portland cement

In ordinary portland cement 100 g. ($100/3.15 = 32 \text{ cm}^3$) will approximately contain 52 g. of tricalcium silicate and 25 g. of dicalcium silicate. This cement can produce CSH, according to equations 2.2 and 2.4 which equals $16+10.2 = 26.2 \text{ cm}^3$.

If cement is hydrate in normal conditions with $w/c = 0.32$, this CSH will have an interlayer water volume 28% of CSH volume according to Mehta⁽²¹⁾, that is $0.28 \times 26.2 = 7.4 \text{ cm}^3$. The adsorbed water⁽¹³⁾ in ordinary portland cement paste is approximately $23 \text{ cm}^3/\text{cement } 100\text{g}$. The capillary water is approximately 0 cm^3 according to the calculation in item 2.2. Then the total volume of water causing shrinkage $7.4+23+0 = 30.4 \text{ cm}^3$.

Expansion of Expansive Agent

Hydration of calcium sulphoaluminate produces ettringite which can be expanded. The volume of ettringite expansion is calculated in equation 2.15 that is, if ettringite volume 30.4 cm^3 is required, then the amount of expansive agent (Calcium sulphoaluminate) should be $13/100 \times 30.4 = 3.89 \text{ cm}^3$ (8.6 g.). This amount of expansive agent can be compensated by the shrinkage which comes from original cement 100 g. The ettringite from tricalcium aluminate is assumed to be transformed into monosulfate aluminate.

Concept of Adjustment

In shrinkage compensating cement, the volume that can be shrunk in portland cement paste is 30.4 cm^3 and it must be compensated by the expansion of ettringite in equal magnitude. The amount of expansive agent can be calculated from the stoichiometric ratio = 8.6 g.

This calculation is approximate due to the limitation of variables that can affect shrinkage. The factors affecting shrinkage are curing temperature, w/c , admixture, moisture content, age of paste, aggregate characteristic and relative humidity.

This research proposed a approximate calculation according to the chemical reaction, the amount of expansive agent in the form of calcium sulphoaluminate can be written as a function of percent of C_3S and C_2S in equation 2.16 ;

$$EA = \alpha_{(t)} 0.2814 \times (0.0861 C_3S + 0.1141 C_2S + W_p) \quad (2.16)$$

Where

EA = amount of expansive agent required to compensate shrinkage (g.)

$\alpha_{(t)}$ = degree of hydration = ratio of hydrated cement to total cement

C_3S = amount of tricalcium silicate in portland cement 100 g. (g.)

C_2S = amount of dicalcium silicate in portland cement 100 g. (g.)

W_p = adsorb water + capillary water (cm^3 .)

In conclusion, ordinary portland cement 100 g. ($32 cm^3$) will approximately contain 52 g. of tricalcium silicate and 25 g. of dicalcium silicate. From this cement with $w/c = 0.32$, the total volume of water causing shrinkage is $30.4 cm^3$. This magnitude of shrinkage will be compensated by using an expansive agent 8.6 g. in the form of calcium sulphoaluminate which can expand an equal magnitude of shrinkage in the paste. But the chemical composition of ordinary cement varies. The same calculation is performed by varying C_3S 45-55% and C_2S 20-30%, resulting in varying the expansive agent 8-15% by the weight of the original cement.

From the theoretical approach, shrinkage compensating cement must have an expansive agent approximately 5-15% to compensate for the shrinkage effects of cement.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย