

## Chapter 3

### Theoretical Background

#### 3.1 General

Carbonation of concrete takes place in the cement paste component. For fly ash concrete, cement paste is the product of the hydration reactions of the cement constituents and pozzolanic reaction of fly ash. When carbon dioxide diffuses into concrete, it dissolves in pore water and thus reacts with calcium hydroxide, which is the product of the hydration reactions. There are several chemical reactions and processes involving the development of concrete and carbonation reaction, which are theoretically discussed in this chapter.

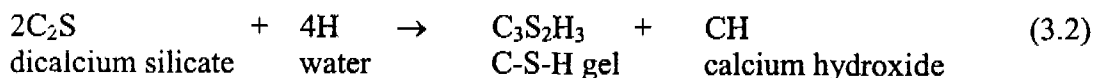
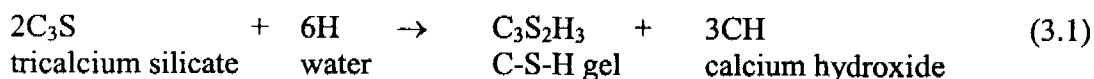
#### 3.2 Hydration and Pozzolanic reactions

##### 3.2.1 Hydration reaction

As soon as water is brought into contact with Portland cement, the cement constituent compounds undergo a series of chemical reactions, called hydration reaction. The hydration reaction produces calcium hydroxide (CH) and the main strength element of hardened cement paste, i.e. calcium silicate hydrate (CSH). Four compounds are usually regarded as the major constituents of cement, i.e. tricalcium silicate ( $C_3S$ ), dicalcium silicate ( $C_2S$ ), tricalcium aluminate ( $C_3A$ ), and tetracalcium aluminoferrite ( $C_4AF$ ). Calcium silicates provide most of CH generated from Portland cement.  $C_3S$  provides most of the CH in early age state, and during the later age (3 to 4 weeks) both  $C_3S$  and  $C_2S$  will equally contribute CH. The chemical reactions taking place are generally complex. However, simple conversions of the main compounds of cement are considered as follows.

##### (i) Calcium silicate hydrates

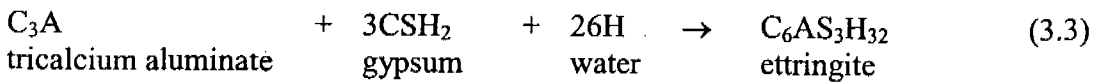
The hydration reactions of the calcium silicates,  $C_3S$  and  $C_2S$ , produce calcium silicate hydrate gels and calcium hydroxide. The hydration reactions of the two calcium silicates make up the largest percent of Portland cement and are the major production of calcium hydroxide in concrete. The representative reactions of the two calcium silicates ( $C_3S$  and  $C_2S$ ) are shown respectively in the following chemical equations.



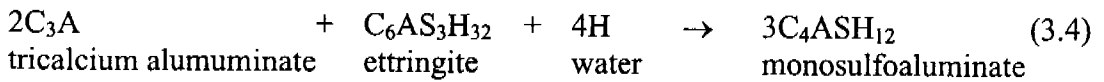
##### (ii) Tricalcium aluminate

The reaction of  $C_3A$  occurs suddenly and makes cement paste rapidly hardened. Therefore, in cement producing process, gypsum is added in order to retard the reaction of this compound.  $C_3A$  reacts with sulfate ions supplied by the dissolved gypsum. The

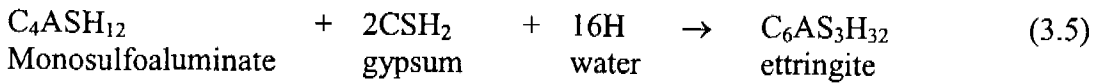
reaction gives calcium sulfoaluminate hydrate (ettringite) as the product. The primary initial reaction of  $C_3A$  is shown as follow.



Ettringite is stable only if there is an ample supply of sulfate. If the sulfate is all consumed before the  $C_3A$  has complete hydrated, then ettringite transforms to monosulfoaluminate as shown as follow.



Monosulfoaluminate forms because there are not sufficient sulfate ions to form the ettringite from the available aluminate ions. If this monosulfoaluminate is brought into contact with a new source of sulfate ions, it reacts to form ettringite as follow.

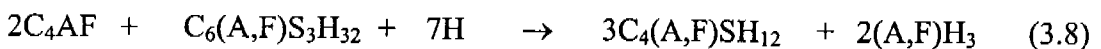
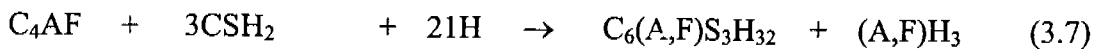


Then, If  $C_3A$  hydrates with no sulfate ions present, then it forms calcium aluminate hydrates as follow.



### (iii) Calcium aluminoferrite

The hydration reactions of  $C_4AF$  are much slower than the  $C_3A$  reactions. As it can be seen in Eq. (3.3a) and Eq. (3.3b) that there is insufficient calcium to form the calcium sulfoaluminates unless the amorphous hydrous oxides of iron or aluminum form also.



### (iv) Effect of fly ash on hydration reaction

It is generally known that in the pozzolanic reaction of fly ash, the  $CH$  produced during cement hydration reacts with the silicate and aluminate phases of fly ash to produce calcium silicate hydrate and calcium aluminate hydrate. However, the cement hydration and the pozzolanic reactions do not proceed independently (Wesche 1991). The interaction between fly ash and cement is a fairly complex phenomenon that involves several independent and interdependent processes. The effect of fly ash on the hydration of cement depends greatly on the chemical and physical nature of the fly ash and water to binder ratio of the mix proportion. (Neville 1995, Seangsoy 2002)

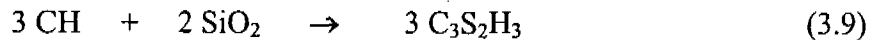
The hydration of  $C_3A$ ,  $C_3S$  and Portland cement appears to be retarded in early stages. The rate of heat evolution is also decreased by fly ash. The initial retardation of  $C_3S$  hydration is due to the aluminate ions and organics dissolved from the fly ash into the aqueous phase of the hydrating system that could delay the nucleation and crystallization

of CH and CSH. The C<sub>3</sub>A hydration retardation was attributed to calcium, sulphate, and alkalis (in addition to organics) dissolved from the fly ash. In addition, the retardation may be caused by the physical effect, in which the fine fly ash particles adhere to the surface of cement grain and consequently obstruct the interaction of cement with water. (Seangsoy 2002)

### 3.2.2 Pozzolanic reaction

Pozzolans or pozzolanic materials are either natural or artificial materials containing siliceous or siliceous and aluminous materials, which themselves process little or no hydration reaction. However, in a finely divided form and in the presence of moisture, these substances can chemically react with CH at ordinary temperature to form CSH compound. The additionally produced CSH compound improves the strength of concrete. This reaction is called the pozzolanic reaction. Fly ash is one of the pozzolanic materials. The pozzolanic reactivity in fly ash is obvious. (Neville 1995)

The components of fly ash are found in both reactively amorphous phases and non-reactively crystallized phases. The primary reaction of pozzolanic material is an attack on the SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> – SiO<sub>2</sub> framework by OH<sup>-</sup> ions. By making a simple assumption that C<sub>3</sub>S<sub>2</sub>H<sub>3</sub> is the main product of the reaction of CH and SiO<sub>2</sub>, the pozzolanic reaction can be simply written as follow.



In addition to the strength gain due to pozzolanic reaction, it is obvious that fly ash improves many properties of concrete. However, the pozzolanic reaction reduces the amount of CH in concrete, lowering the alkalinity of concrete and therefore the durability of concrete structures due to the carbonation reaction is considerably reduced. CH liberated from the hydration reaction combines chemically with the reactive component of fly ash to form stable calcium silicates.

### 3.2.3 Degree of hydration and pozzolanic reactions

The degree of hydration of each cement compound (C<sub>3</sub>A, C<sub>3</sub>S, C<sub>2</sub>S, and C<sub>4</sub>AF) can be defined as the function of ratio of cumulative heat generated up to the time considered to the maximum cumulative heat generation of each mineral compound in cement. Seangsoy (2002) proposed empirical formulas for determining the degree of hydration of each cement compound as the function of water to cement ratio, temperature, and age of the concrete (see Appendix A). Examples of the degree of hydration reactions of all cement compounds are shown in Fig. 3.1.

Under a simple assumption that hydration process of each cement compound (C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A, C<sub>4</sub>AF) is independent, the average degree of hydration of cement was defined as the weight average of the rate of hydration of its constituents as follow.

$$\alpha_{hy}(t) = \frac{\sum_{i=1}^4 m_i \alpha_i(t)}{\sum_{i=1}^4 m_i} \quad (3.10)$$

where  $\alpha_{hy}(t)$  is the average degree of hydration of cement (%).  $i$  is the mineral compound of cement ( $C_3S$ ,  $C_2S$ ,  $C_3A$ ,  $C_4AF$ ).  $m_i$  is the mass of each compound per cubic meter of cement ( $kg/m^3$ ).  $\alpha_i(t)$  is the degree of hydration (%) of each compound in cement (see Appendix A).

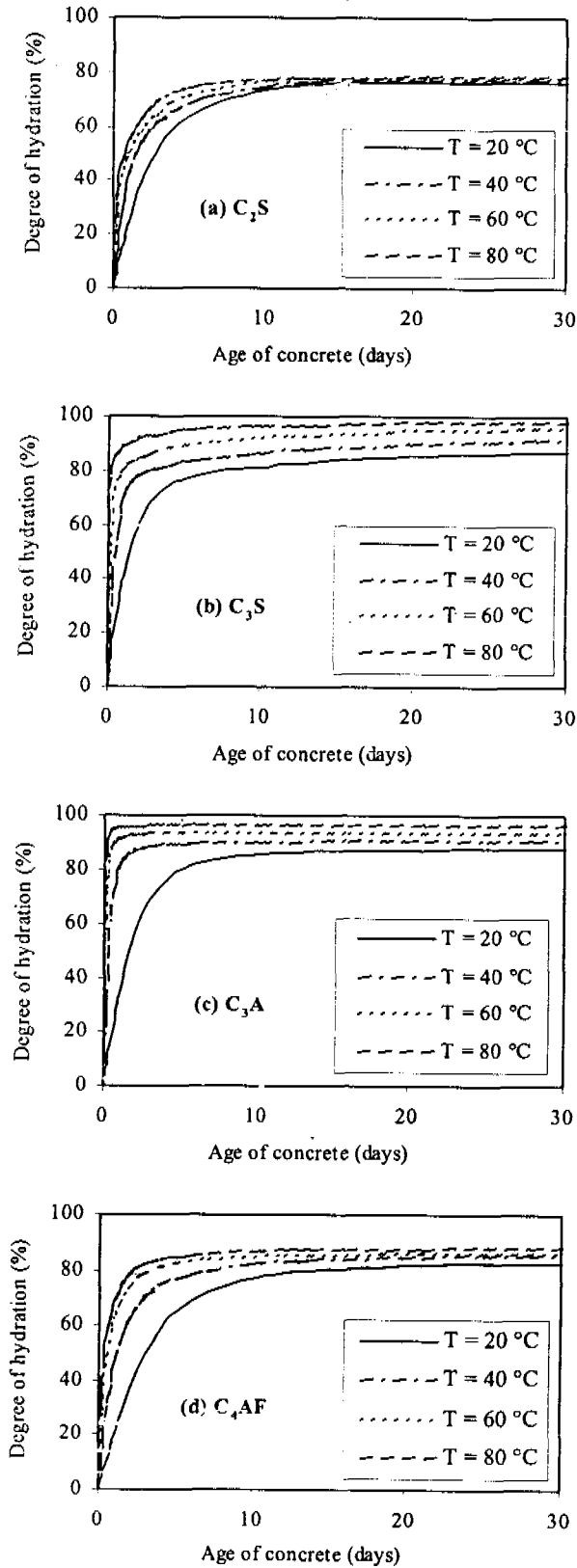


Fig. 3.1 Degree of hydration of the mineral components in cement (%)

Seangsoy (2002) also defined the pozzolanic reaction as the weight fraction of already reacted fly ash per total fly ash in the paste mixture. The degree of pozzolanic reaction was considered affected by water to binder ratio, properties of binder materials, temperature, and age of the concrete (see Appendix A). An example of the degree of pozzolanic reaction is shown in Fig. 3.2.

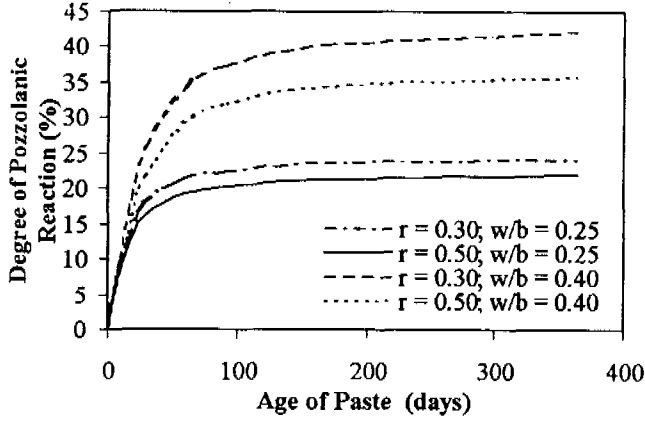


Fig. 3.2 Degree of pozzolanic reaction (%)

The average degree of reaction of cement and fly ash is defined in this study as the weight fraction average of the average degree of hydration of cement and the degree of pozzolanic reaction of fly ash as follow.

$$\alpha_{av} = (1 - r) \alpha_{hy} + r \alpha_{poz} \quad (3.11)$$

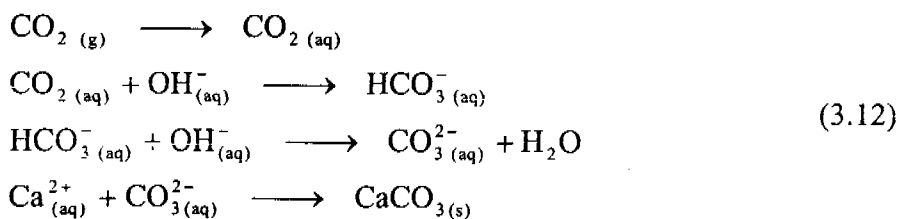
where  $\alpha_{av}(t)$ ,  $\alpha_{hy}(t)$ ,  $\alpha_{poz}(t)$  are the average degree of reaction of cement and fly ash, average degree of hydration of cement, and degree of pozzolanic reaction of fly ash, respectively (%) at time  $t$  (day).  $r$  is the fly ash to total binder ratio.

### 3.3 Carbonation Reaction

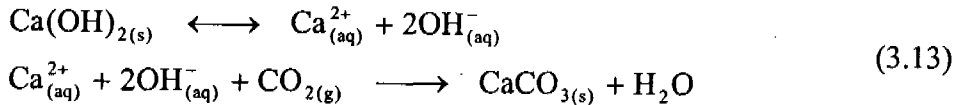
#### 3.3.1 Carbonation reaction

Carbonation occurs when carbon dioxide present in the atmosphere reacts, in the presence of moisture, with calcium hydroxide release form hydration reaction. The reaction occurs in either gas phase or aqueous phase of carbon dioxide as can simply be described by the following chemical equations.

(i) Carbonation reaction in aqueous phase



### (ii) Carbonation reaction in gas phase



Since air is in direct contact with the external surface of concrete, the exposed surface is carbonated very quickly after the first exposure. As air enters the interconnected capillary pores of the concrete, the carbon dioxide contained in the air is rapidly used up by the reaction with hydroxides. In this condition there is a movement of carbon dioxide from air outside towards the depleted air inside in an attempt to restore a uniform concentration. This movement from a high concentration to a low concentration is called diffusion. However, carbon dioxide reacts rapidly with the hydroxides it can not easily move past the barrier of non-carbonated concrete until all the hydroxide has been consumed. For this reason the carbonated layer is also defined. (Mays 1992)

Carbonation also results in an increase of strength and a reduction of permeability. This is because calcium carbonate produced by carbonation reaction reduces the voids within the carbonated cement paste. However, the increase of strength is not structurally significant. The protection of steel by the alkaline condition of hydrated cement paste is depleted by carbonation. Thus if the entire concrete cover to steel is carbonated, corrosion of steel can occur during the ingress of moisture and oxygen. This is clearly of critical significance. (Neville 1995)

### 3.3.2 Arrhenious's formulation and rate of carbonation reaction

It is generally known that as the ambient temperature increases, a given chemical reaction will proceed faster. Quantitatively this relationship between the rate of reaction and its temperature is determined by the Arrhenious's equation. At higher temperatures, there is a probability that the molecules of two substances will collide more. This higher collision rate results in a higher kinetic energy, which has an effect on the activation energy of the reaction. The activation energy is the amount of energy required to ensure that a reaction happens. In order to evaluate rate of carbonation reaction, the Arrhenious's equation of reaction is adopted. The Arrhenious's equation is given as follow.

$$k_c = \beta \exp\left[-\frac{E_0}{RT}\right] \quad (3.14)$$

where  $k_c$  is the reaction rate coefficient.  $\beta$  is the constant for the reaction that is in the same unit as  $k_c$ .  $E_0$  is the Arrhenious activation energy of the reaction.  $R = 8.2 \times 10^{-5} \text{ m}^3 \cdot \text{atm/mol/K}$  ( $8.3 \text{ J/mol/K}$ ) is the gas constant.  $T$  is temperature ( $^{\circ}\text{K}$ ).

### 3.4 Diffusion and Gas Transport Mechanism

The ingress of gases, water or ions in a aqueous solution, into concrete takes place through pore spaces in the cement paste matrix or micro cracks. The transport of these substances into concrete depends on pore characteristics of concrete, width of micro crack, degree of saturation of the pore system, aggregate content, and temperature. Transfer of mass by random motion of free molecules or ions in the pore solution results in a net flow

from regions of higher concentration to regions of lower concentration of the diffusion substance. The rate of transfer of mass through a unit area of a section is proportional to the concentration gradient and the diffusion coefficient. This relation can be expressed by Fick's first law of diffusion as follow. (Kropp and Hilsdorf 1995)

$$F = -D \frac{\partial c}{\partial x} \quad (3.15)$$

where F is the mass flux ( $\text{kg/m}^2 \cdot \text{s}$ ). D is the diffusion coefficient ( $\text{m}^2/\text{s}$ ). c is the concentration ( $\text{kg/m}^3$ ). x is the distance (m). In porous solids, such as concrete, moisture moves in the form of diffusion of water vapor and hydraulic pressure. However at the same time, non-saturated or even saturated capillary flow may occur in finer pores. Although additional transport mechanisms are acting in these cases, Fick's law of diffusion can be applied to quantify the multiple transport cases, especially near the exposed surface of concrete since capillary movement occurs in a very short period of time (Rose 1965). A concentration gradient is considered as the common driving force. The diffusion coefficient depends on material properties at that condition. For transient diffusion processes the balance equation describes the changes of concentration in a unit volume with time (t). This relation is referred to as Fick's second law of diffusion as follow. (Bazant and Najjar 1972)

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \quad (3.16)$$

### 3.5 Henry's Law and Solubility of Gases

The solubility of a gas in a liquid, i.e. carbon dioxide dissolves in pore water, depends on temperature, the partial pressure of the gas over the liquid, the nature of the solvent and the nature of the gas. The most common solvent is water. Gas solubility is always limited by the equilibrium between the gas and a saturated solution of the gas. The concentration of dissolved gas depends on the partial pressure of the gas above the solvent. The partial pressure controls the number of gas molecule collisions with the surface of the solution. If the partial pressure is double, the number of collisions with the surface will double. The increased numbers of collisions produce more dissolved gas. Therefore, if the temperature stays constant, increasing the pressure will increase the amount of dissolved gas. The Henry's constant for the equilibrium of gas dissolving in liquid is defined as follow.

$$H = \frac{P}{C} \quad (3.17)$$

where H is the Henry's constant ( $\text{atm} \cdot \text{m}^3/\text{mol}$ ). P is the partial pressure of the gas (atm). C is the molar concentration of the gas ( $\text{mol/m}^3$ ). Henry's law is found to be an accurate description of the behavior of gases dissolving in liquids when concentrations and partial pressures are reasonably low. As concentrations and partial pressures increase, deviations from Henry's law become noticeable. This behavior is very similar to the behavior of gases, which are found to deviate from the ideal gas law as pressures increase and temperatures decrease.

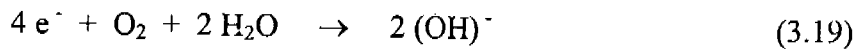
### 3.6 Mechanisms of Steel Corrosion

Mechanisms of steel corrosion can be divided into two processes, which are anodic and cathodic processes. Naturally reinforcing steel in concrete is prevented from corrosion by the high alkalinity of concrete. This is because reinforcing steel is not able to dissolve into steel ion and electron (anodic process cannot happen). Corrosion of steel will start when the alkalinity of concrete cover to reinforcement is neutralized to the critical level with the presence of moisture and oxygen.

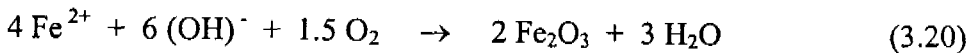
When the passive protective oxide film around reinforcing steel has been depassivated until the critical point is reached, the reinforcing steel is able to dissolve into ferric ion ( $\text{Fe}^{2+}$ ) and electron ( $2e^-$ ) as shown below. This reaction is called the anodic reaction.



Thereafter, the released electron from the anodic process combines with moisture and oxygen to produce hydroxyl ions. Since, the electron dissolved from the anodic reaction can move along the steel. This process can occur even at the places where the surrounding concrete is not depassivated.



After the anodic and the cathodic process have occurred for some stages,  $\text{Fe}^{2+}$  and  $\text{OH}^-$  will combine to form rust in steel ( $\text{Fe}_2\text{O}_3$ ) as shown as in the following.



As the result from the corrosion of reinforcing steel, the cross-sectional area at the anode of the steel is reduced and the rust, which has approximately six times more volume than the dissolved steel, causes the splitting crack in the concrete cover.