

Modeling of chloride diffusion in a hydrating concrete incorporating silica fume

Xiao-Yong Wang¹, Ki-Bong Park¹ and Han-Seung Lee*²

¹Department of Architectural Engineering, College of Engineering, Kangwon National University, Chuncheon, 200-701, Korea

²School of Architecture & Architectural Engineering, Hanyang University, Ansan, 425-791, Korea

(Received October 30, 2011, Revised January 18, 2012, Accepted May 23, 2012)

Abstract. Silica fume has long been used as a mineral admixture to improve the durability and produce high strength and high performance concrete. And in marine and coastal environments, penetration of chloride ions is one of the main mechanisms causing concrete reinforcement corrosion. In this paper, we proposed a numerical procedure to predict the chloride diffusion in a hydrating silica fume blended concrete. This numerical procedure includes two parts: a hydration model and a chloride diffusion model. The hydration model starts with mix proportions of silica fume blended concrete and considers Portland cement hydration and silica fume reaction respectively. By using the hydration model, the evolution of properties of silica fume blended concrete is predicted as a function of curing age and these properties are adopted as input parameters for the chloride penetration model. Furthermore, based on the modeling of physicochemical processes of diffusion of chloride ion into concrete, the chloride distribution in silica fume blended concrete is evaluated. The prediction results agree well with experiment results of chloride ion concentrations in the hydrating concrete incorporating silica fume.

Keywords: silica fume; chloride; diffusion; simulation; durability.

1. Introduction

Silica fume (SF) is a byproduct of the induction arc furnaces in the silicon metal and ferrosilicon alloy industries. It is a highly pozzolanic cement replacement material because it consists essentially of silica in noncrystalline form with a high specific surface. It is mainly used to improve the workability and durability of concrete. In addition, due to energy-saving and resource-conservation, both ecological and economical benefit can be achieved by using silica fume blended Portland cement (Mehta 2006).

It is widely known that the ingress of chloride ions constitutes a major source of durability problems affecting reinforced concrete structures which are exposed to saline environments. Once a sufficient quantity of chloride ions has accumulated around the embedded steel, pitting corrosion of the metal is liable to occur unless the environmental conditions are strongly anaerobic. In the design of concrete structures, the influence of chloride ingress on service life must be considered (Mehta 2006).

The literature is rich in papers dealing with chloride attack of concrete. Papadakis (2000) and Papadakis *et al.* (1996a) made experimental investigations and theoretical modeling of chloride ingress into concrete incorporating silica fume. The physicochemical processes of diffusion of

* Corresponding author, Professor, E-mail: ercleehs@hanyang.ac.kr

chloride ion in the aqueous phase of pores, their adsorption and binding in the solid phase of concrete were described by a nonlinear partial differential equation. Based on computed micro pore structure (Breugel 1995), Yoon (2009) proposed a simple approach to calculate the diffusivity of concrete considering carbonation. The parameters affecting the chloride diffusivity, such as the diffusivity in pore solution, tortuosity, micro-structural properties of hardened cement paste, and volumetric portion of aggregate, are taken into consideration in the calculation of chloride diffusivity. Han (2007) proposed a modified diffusion coefficient that considers the effect of chloride binding and evaporable water on the diffusion coefficient. The evaporable water content was predicted from a hydration model of Portland cement. Based on mathematical derivation of microstructure of concrete, Song *et al.* (2007) built a procedure for predicting the diffusivity of high strength SF concrete. In this model the influence of water to binder ratio, SF replacement ratio, and degree of hydration on diffusivity was considered. Ishida *et al.* (2009) formulated the chloride diffusivity based on computed multi-scale micro-pore structure, which considers tortuosity and constrictivity of porous network as reduction factors in terms of complex micro-pore structure and electric interaction of chloride ions and pore wall. From references (Papadakis *et al.* 1996a, Papadakis 2000, Yoon 2009, Han 2007, Song *et al.* 2007, Ishida *et al.* 2009), we can see that based on a hydration model, the evolution of concrete properties, such as the content of evaporable water and porosity, can be described as a function of curing age. The diffusivity of chloride ions in concrete can be obtained from the microstructure of concrete.

Due to the pozzolanic reaction between calcium hydroxide and silica fume, compared with ordinary Portland cement, hydration of concrete containing silica fume is much more complex. It is difficult to build a chemical-based kinetic equation to quantitatively describe the evolution of properties of silica fume blended concrete and only the final concentrations of reaction products, which apply after the Portland cement hydration and pozzolanic reaction are complete and a steady is established (Papadakis 2000, Papadakis *et al.* 1992).

In this paper, a numerical procedure which can simulate chloride diffusion in silica fume blended concrete is built. The flow chart of this procedure is shown in Fig. 1. As shown in Fig. 1, this

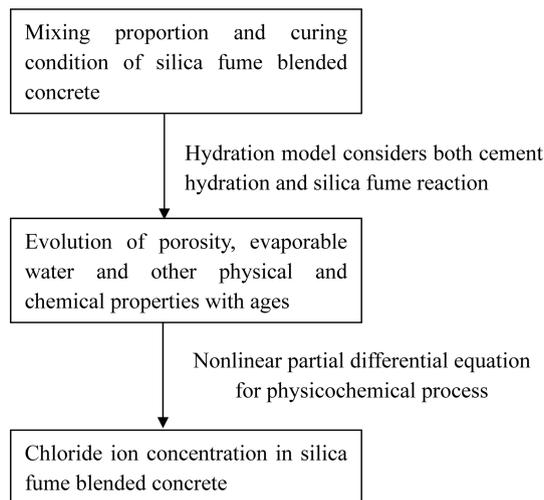


Fig. 1 The flow chart of predicting chloride ion concentration in silica fume blended concrete

numerical procedure includes a hydration model and a chloride diffusion model. In the hydration model, by considering the producing of calcium hydroxide in cement hydration and the consumption of it in pozzolanic reaction, a numerical model is proposed to simulate the hydration of concrete containing silica fume. The contents of evaporable water, calcium hydroxide and porosity were obtained as companied results of the hydration model and were used as input variables for the chloride diffusion model. Furthermore, in the chloride diffusion model, the physicochemical processes of diffusion of chloride ion in the aqueous phase of pores, the adsorption and binding in the solid phase of concrete, and the desorption are described by a nonlinear partial differential equation. The proposed chloride penetration profiles were verified with the experimental results.

2. Hydration model of portland cement

2.1 The assumptions of the hydration model

In this hydration model, the influences of the water to cement ratio, cement particle size distribution, cement mineral components and curing temperature on the hydration reaction of Portland cement are considered. The assumptions of this model can be summarized as follows:

1. Cement particles are randomly cast in a representative unit cell space, as shown in Fig. 2. As proposed by Navi and Pignat (1996), the length of the edge of the representative unit cell is 100 microns. The amount of chemically bound water for each cement component, C_3S , C_2S , C_3A and C_4AF , proposed by Park *et al.* (2005) is used for the simulation in this paper.

2. The degree of hydration of cement components is the ratio of the volume of reacted cement components to the volume of initial cement components. The degree of the hydration of cement paste can be regarded as a weighted sum of cement particles and mineral components as shown in Fig. 3.

3. The liquid phase, which is assumed to be water, diffuses through a hydrate layer, reaches the surface of the cement particle and chemically reacts with cement. The hydrate formed by hydration adheres to the cement particles spherically.

4. Particle size distribution of cement can be approximated using the Rosin-Rammler function (Park *et al.* 2005).

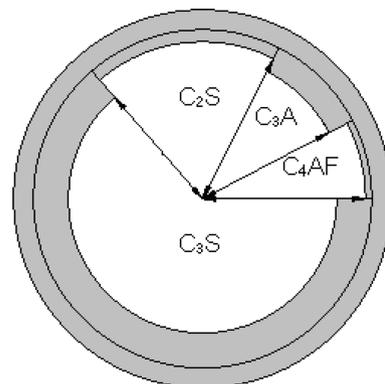
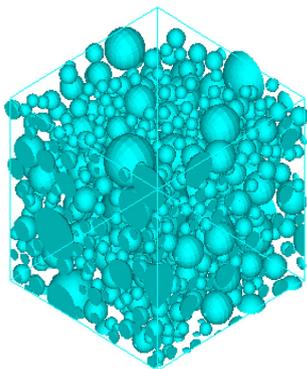


Fig. 2 Cement particles distribute randomly in cell space Fig. 3 The schematic of multi-component hydration model

2.2 Hydration mechanism

In Park's model (2005), some improvements were achieved by incorporating the size distribution of cement particles and the component of cement minerals, including C₃S, C₂S, C₃A and C₄AF. The basic hydration equation for each mineral composition in cement particles can be described as Eq. (1), which is originally built by Tomosawa (1997) to describe the hydration of a single cement particle. This model is expressed as a single equation composed of four rate determining coefficients, which consider the rate of formation and destruction of initial impermeable layer, the activated chemical reaction process, and following diffusion-controlled process

$$\frac{d\alpha_i^j}{dt} = \frac{3\rho_w}{(v_i + w_{ag})r_0^j \rho_i \left(\frac{1}{k_d} - \frac{r_0^j}{D_{ei}} \right) + \frac{r_0^j}{D_{ei}} (1 - \alpha_i^j)^{-\frac{1}{3}} + \frac{1}{k_{ri}} (1 - \alpha_i^j)^{-\frac{2}{3}}} \quad (1)$$

where α_i^j denotes the hydration degree of the mineral component in given cement particle; i is the mineral component; j is the number of cement particles; v_i is the stoichiometric ratio by the mass of water to mineral component; w_{ag} is the physically bound water that is approximately equal to 15% of the mass of reacted cement; ρ_i is the density of the anhydrate cement mineral component; k_d is the reaction coefficient in a dormant period; r_0^j is the radius of anhydrate cement particles; D_{ei} is the effective diffusion coefficient of water in the hydration product for each mineral component; k_{ri} is the coefficient of reaction rate for each mineral component and ρ_w is the density of water.

Whereas, k_d is assumed to be a function of the degree of hydration during the initial reaction period. It is expressed as Eq. (2)

$$k_d = \frac{B}{(\alpha_i^j)^{1.5}} + C(r_0^j - r_i^j)^4 \quad (2)$$

The B and C in Eq. (2) denote reaction coefficients.

The effective diffusion coefficient of water is affected by the tortuosity of the gel pore as well as the radius of the gel pore in the hydrate. This phenomenon can be expressed as a function of the degree of hydration and is described by Eq. (3)

$$D_{ei} = D_{ei0} \ln\left(\frac{1}{\alpha_i^j}\right) \quad (3)$$

The influence of temperature on cement hydration is considered by Arrhenius law (Park 2005) as Eqs. (4)-(6)

$$B = B_{20} \exp\left(-\beta_1 \left(\frac{1}{T} - \frac{1}{293}\right)\right) \quad (4)$$

$$D_{ei} = D_{ei20} \exp\left(-\beta_{2i} \left(\frac{1}{T} - \frac{1}{293}\right)\right) \quad (5)$$

$$k_{ri} = k_{ri20} \exp\left(-\frac{E_i}{R} \left(\frac{1}{T} - \frac{1}{293}\right)\right) \quad (6)$$

where B_{20} , D_{ei20} and k_{ri20} are the values of B , D_{ei} and k_{ri} at 293K respectively, and β_1 , β_{2i} and E_i/R

are the activation energies of B , D_{ei} and k_{ri} respectively. The activation energies of each compound are obtained from the cement hydration experiments performed under different curing temperatures.

When the cement is mixed with water, the hydration of each mineral component processes according to the model described in the previous section. The degree of the hydration of cement can be calculated as Eq. (7)

$$\alpha = \frac{\sum_{j=1}^{m} \sum_{i=1}^4 \alpha_i^j g_i g_j}{\sum_{j=1}^{m} \sum_{i=1}^4 g_i g_j} \quad (7)$$

where α is the degree of hydration of cement g_i is the mass fraction in mineral components; g_j is the mass fraction of individual particle in cement and m is the total number of cement particles in a cell space. As shown in Eq. (7), the different hydration reactions do not consume the same amount of water, so the computation of the total consumed water should be a weighted average of the consumed water for each elementary reaction.

2.3 Water withdrawal mechanism

During the hydration period, at a certain time point after the initial setting time, due to the increasing interconnection among cement particles, the contact area between cement particle and surrounding water will be decreased. As a result, a slower hydration rate will be achieved. On the other hand, the water presenting in the paste can be classified into evaporable and non-evaporable fractions (Park *et al.* 2005). The former is the capillary water and the gel water that resides partially within the hydration product. The non-evaporable water is defined as the bound water which has chemically reacted with cement. During the hydration process, only the capillary water contributes to further hydration. With the hydration process proceeding, the capillary water will be consumed and the relative hydration rate will decrease. In this paper, it is assumed that under conditions of sealed-curing, when the water-to-cement ratio is less than 0.38, due to a limited amount of available water, cement hydration is not complete (Park *et al.* 2005). (The mass of chemically bound water approximately equals 23% of the mass of reacted cement and the mass of gel water approximately equals 15% of the mass of reacted cement.)

By considering these two points, as proposed by Park *et al.* (2005) and Maruyama *et al.* (2005), the modification of Eq. (1) can be expressed as Eq. (8)

$$\left(\frac{d\alpha_i^j}{dt}\right)' = \frac{d\alpha_i^j}{dt} \times \left(\frac{\text{freesurface}}{\text{totalsurface}}\right)^j \times \frac{\text{capillarywater}}{w_0} \quad (8a)$$

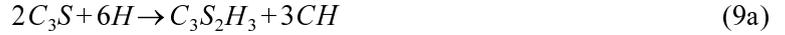
$$\text{capillarywater} = w_0 - 0.38 \times C_{e_0} \times \alpha \quad (8b)$$

In Eq. (8a), the item $\left(\frac{\text{freesurface}}{\text{totalsurface}}\right)^j$ is the ratio between the free surface area (the area which contacts with water) and the total surface area, which can be determined by the proposed method in reference (Navi and Pignat 1996). w_0 is the water mass and C_{e_0} is the cement mass in a mixing proportion. The item $\frac{w_0 - 0.38 \times C_{e_0} \times \alpha}{w_0}$ represents the decrease of available capillary water for cement hydration.

3. Hydration model for cement blended with silica fume

3.1 The amount of calcium hydroxide (CH) during the hydration process

As proposed by Papadakis (1999a, 1999b), during the hydration period, the chemical reaction of the mineral components of Portland cement can be expressed with the following Eqs. (9a)-(9d)

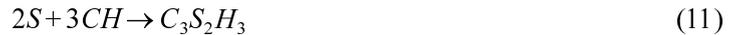


The Eqs. (9a)-(9d) can be used to determine the final chemical and volumetric composition of Portland cement concrete. On the other hand, based on the experimental investigation on calcium hydroxide amount and degree of hydration of cement, Sakei and Monteiro (2005) and Pane and Hansen (2005) reported that during the hydration process of cement paste, the amount of calcium hydroxide is linearly dependent on the degree of hydration of cement. Hence, by the combination Papadakis' chemical equation with the degree of hydration of cement, the mass of calcium hydroxide in a unit volume of concrete can be obtained as following Eq. (10)

$$CH = (0.49 \times g_{c_{3s}} + 0.22 \times g_{c_{2s}} - 0.3 \times g_{c_{4af}}) \times Ce_0 \times \alpha \quad (10)$$

Where $g_{c_{3s}}$, $g_{c_{2s}}$ and $g_{c_{4af}}$ is the weight fraction of the mineral component C_3S , C_2S and C_4AF respectively.

Silica fume is composed primarily of $SiO_2(S)$, which is almost completely vitreous. It also contains a small amount of carbon and very small amounts of other compounds. Based on the experimental results of the reaction stoichiometry among silica fume, chemical bound water and calcium hydroxide, Papadakis (1999a) proposed that the pozzolanic reaction in cement-silica fume blends can be written as following Eq. (11)



During the hydration period of cement blended with silica fume, considering the effect of pozzolanic reaction, the mass of calcium hydroxide can be rewritten as Eq. (12)

$$CH = (0.49 \times g_{c_{3s}} + 0.22 \times g_{c_{2s}} - 0.3 \times g_{c_{4af}}) \times Ce_0 \times \alpha - 1.85 \times \alpha_{silica} \times m_{silica0} \times \gamma_s \quad (12)$$

In Eq. (12), α_{silica} is the degree of hydration of the glass (active) phase of silica fume; $m_{silica0}$ is the silica fume mass in mixing proportion; γ_s is the mass percentage of glass silica in silica fume. In Eq. (12), the term $(0.49 \times g_{c_{3s}} + 0.22 \times g_{c_{2s}} - 0.3 \times g_{c_{4af}}) \times Ce_0 \times \alpha$ considers the producing of calcium hydroxide from cement hydration and the term $-1.85 \times \alpha_{silica} \times m_{silica0} \times \gamma_s$ considers the consumption of it in pozzolanic reaction.

Similar with the hydration of cement, with the proceeding of pozzolanic reaction, the water will be physically adsorbed in the hydration products of silica fume. Jensen and Hansen (2001) proposed that for the silica fume pozzolanic reaction, when 1 g silica fume reacts, 0.5 g gel water and 0 g chemical water will be consumed. Hence the mass of capillary water and chemically bound water in hydrating cement-SF blends can be rewritten as following Eqs. (13a) and (13b)

$$w_{cap} = w_0 - (0.23 \times C_{e_0} \times \alpha + 0.15 \times C_{e_0} \times \alpha) - 0.5 \times \alpha_{silica} \times m_{silica0} \times \gamma_s \quad (13a)$$

$$w_{chem} = 0.23 \times C_{e_0} \times \alpha \quad (13b)$$

Where w_{cap} and w_{chem} is the mass of capillary water and chemically bound water, respectively. In Eqs. (13a) and (13b), the term $(0.23 \times C_{e_0} \times \alpha + 0.15 \times C_{e_0} \times \alpha)$ considers the reduction of capillary water due to cement hydration. The term $0.5 \times \alpha_{silica} \times m_{silica0} \times \gamma_s$ considers the reduction of capillary water due to pozzolanic reaction. Compared with Portland cement, the physically bound water within silica fume hydration products is much higher. This maybe comes from the relatively higher CSH content in silica fume hydration products (Jensen and Hansen 2001).

3.2 The simulation of pozzolanic reaction in cement-silica fume blends

The proposed model comes from the similarity in mechanism between cement hydration and pozzolanic activity: Firstly, the cement reacts with water and the glass phase of pozzolanic material reacts with calcium hydroxide. The cement hydration process includes initial dormant period, phase-boundary reaction period and diffusion period. In the late age of cement hydration, diffusion is the control process. Some researchers reported that pozzolanic activity was a diffusion-controlled process (Papadakis 1999a, 1999b). Secondly, based on the analysis of SEM micrographs of Portland cement paste, silica fume-cement paste and fly ash-cement paste, Papadakis (1999a, 1999b) reported that the cement hydration product adheres on surface of unreacted cement particles and the pozzolanic product adheres on surface of unreacted pozzolanic particles. Thirdly, the cement particle with small size has a highly reactivity with water and almost shows no initial dormant period and the cement particle with big size shows an initial dormant period (Park *et al.* 2005). Similarly, silica fume is a highly pozzolanic cement replacement material and shows almost no initial dormant period, like small cement particle. Fly ash shows a long initial dormant period. On the other hand, there also exist some differences between cement hydration and pozzolanic activity. Cement hydration will produce calcium hydroxide and pozzolanic activity will consume it. The hydration rate of pozzolanic materials depends on the amount of calcium hydroxide in hydrating blends and the degree of hydration of the mineral admixture (Sakei and Monteiro 2005, Maruyama *et al.* 2005). So we can deduce an equation from cement hydration to pozzolanic reaction by considering both similarity and difference between two reactions.

Because of the high specific surface of silica fume and great pozzolanic activity, in this paper it is assumed that the hydration of silica fume includes two processes: phase-boundary reaction process and diffusion process. Considering these points, based on the proposed method by Saeki and Monteiro (2005), the hydration equation of silica fume can be written as Eq. (14a)

$$\frac{d\alpha_{silica}}{dt} = \frac{m_{CH}(t)}{m_{silica0} v_{si} r_{si0} \rho_{si}} \frac{3\rho_w}{\frac{r_{sio}}{D_{esi0}} (1 - \alpha_{silica})^{\frac{-1}{3}} - \frac{r_{si0}}{D_{esi0}} + \frac{1}{k_{rsi}} (1 - \alpha_{silica})^{\frac{-2}{3}}} \quad (14a)$$

Where $m_{CH}(t)$ is the calcium hydroxide mass in a unit volume in hydrating cement-silica fume blends and can be obtained from Eq. (12). v_{si} is the stoichiometry ratio by mass of CH to silica fume. r_{sio} is the radius of silica fume particle. ρ_{si} is the density of silica fume. D_{esi0} is the diffusion coefficient and k_{rsi} is the reaction rate coefficient.

The influence of temperature on hydration is considered by Arrhenius law as following Eqs. (14b)

and (14c)

$$k_{rsi} = k_{rsi20} \exp[-E_{si}/R(1/T-1/293)] \quad (14b)$$

$$D_{esi0} = D_{esi20} \exp[-\beta_{esi}(1/T-1/293)] \quad (14c)$$

Where k_{rsi20} and D_{esi20} are reaction coefficients at 20°C; E_{si}/R and β_{esi} are activation energies. The heat evolution rate of hydrating cement-silica fume blends consists of contribution from two parts: the heat generated from Portland cement hydration and the heat generated from pozzolanic reaction between silica fume and calcium hydroxide.

Papadakis (1999a, 1999b) evaluated the total porosity of concrete by considering the contribution from cement hydration and pozzolanic reaction. Based on the stoichiometry of the reactions and the differences in volumes between the solid reactants and solid products, the total porosity can be evaluated as following

$$\varepsilon = \frac{w_0}{\rho_w} - \Delta\varepsilon_h - \Delta\varepsilon_p \quad (15)$$

Where $\Delta\varepsilon_h$ is porosity reduction due to hydration of Portland cement, which equals to the reduction of chemical bound water during hydration process. $\Delta\varepsilon_p$ is porosity reduction due to pozzolanic activity (as proposed in reference (Papadakis 1999a), $\Delta\varepsilon_p$ is very small and can be regarded as zero).

4. Verification of the hydration model

4.1 The degree of hydration of mineral components of Portland cement

The results of this part in the experiments for regarding the hydration degree of ordinary Portland cement were used (Matsushita *et al.* 2007). The mineral compositions of cement are given as C₃S 63.3%, C₂S 10.3%, C₃A 9.1% and C₄AF 9.2%, respectively. The water to cement ratio was 0.5 and curing temperature was 10°C, 20°C and 40°C. The hydration degree of the mineral components was measured at 1, 3, 7, 28, 91, 190 and 365 days. Powder X-Ray diffraction/Rietveld analysis was used to measure the degree of hydration of cement mineral components.

By regression experimental results (Matsushita *et al.* 2007), the reaction coefficients of the multi-components hydration model were obtained and listed in Table 1. The comparison between the experiment results and the prediction results was shown in Fig. 4. Because the reaction rate of C₃S and C₃A is much quicker than C₂S and C₄AF, the hydration of C₃S and C₃A reaches a steady state much earlier than C₂S and C₄AF. Most of C₃A and C₃S have reacted in the first 1000 hours. As

Table 1 The hydration coefficients of proposed model

B	C	k_{rc3s}	k_{rc2s}	k_{rc3a}	k_{rc4af}	De_{c3s0}	De_{c3a0}	De_{c2s0}	De_{c4af0}
2E-9	1.5E15	2.422E-5	1.815E-7	1.985E-6	3.759E-7	6.328E-10	9.568E-8	6.328E-10	9.568E-8
β_1	$\frac{E_{c3s}}{R}$	$\frac{E_{c2s}}{R}$	$\frac{E_{c3a}}{R}$	$\frac{E_{c4af}}{R}$	β_{2c3s}	β_{2c3a}	β_{2c2s}	β_{2c4af}	
89	6000	3500	7000	3000	3500	4500	3500	4500	

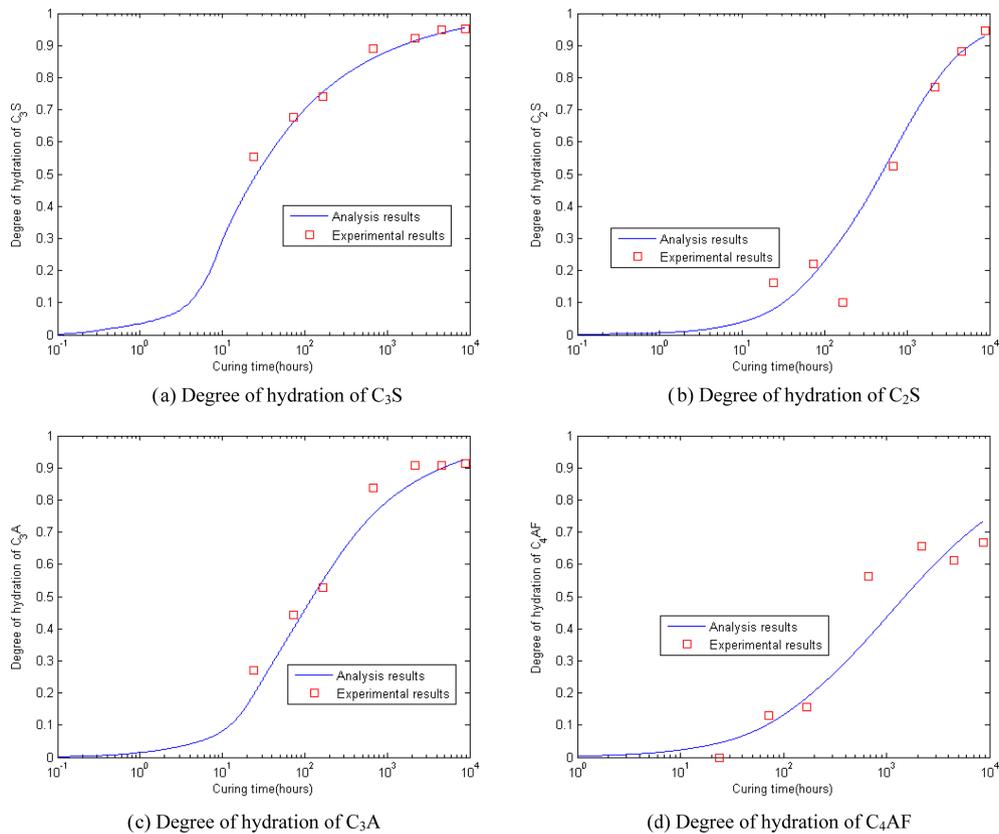


Fig. 4 The comparison between experimental results (Matsushita 2007) and simulation results of hydration degree of cement mineral components: C_3S , C_2S , C_3A and C_4AF ($W/C=0.5$, Curing temperature= $20^\circ C$)

shown in Fig. 4, the prediction results overall agree well with experimental results (Matsushita *et al.* 2007).

From the degree of hydration of the individual mineral components, we can predict the degree hydration of cement with different water to cement ratios and curing temperatures. As shown in the Fig. 5, the evaluation results are generally agree with experimental results (Matsushita *et al.* 2007) on hydration ratio of cement cured at $10^\circ C$, $20^\circ C$ and $40^\circ C$ and with water to cement ratio 0.5, 0.35 and 0.25. As shown in Fig. 5, the tendencies of acceleration by high temperature curing, retardation by low temperature curing and reduction in the reaction rate by reduction in the water to cement ratio are recognized. As shown in Fig. 5(a), acceleration and retardation of the reaction of cement depending on the curing temperature are evened out at 190 days at a reaction degree of 85-90%, and the ultimate degree of hydration of cement with different curing temperatures tends to be same. As shown in Fig. 5(b), the effect of losses in the water and deposition spaces necessary for hydration due to a low W/C is recognized after an age of 1 and 3 days with a W/C of 25% and 35%, respectively.

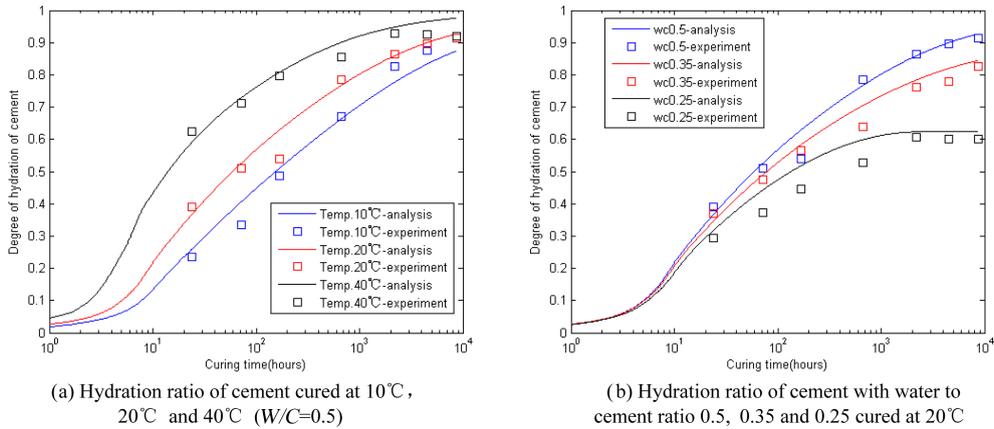


Fig. 5 The prediction of degree hydration of cement with different water to cement ratios and curing temperatures (experimental results are from reference (Matsushita 2007))

Table 2 Mixture proportions for specimens

Specimen	Cement (kg/m ³)	Water (kg/m ³)	Silica fume (kg/m ³)	Aggregate (kg/m ³)	Water to cement ratio	Silica fume to cement ratio	Aggregate to cement ratio
Control	514.6	257.4	0.0	1543.8	0.5	0.0	3.0
SFA1	514.6	257.4	25.7	1513.4	0.5	0.05	2.94
SFA2	514.6	257.4	51.5	1483.0	0.5	0.1	2.88
SFA3	514.6	257.4	77.2	1452.6	0.5	0.15	2.82
SFC1	488.8	257.4	25.7	1535.3	0.527	0.053	3.14
SFC2	463.1	257.4	51.5	1526.9	0.556	0.111	3.30
SFC3	437.4	257.4	77.4	1518.4	0.588	0.176	3.47

4.2 Hydration process of cement blended with silica fume

In this part, the experimental results of the hydration of cement-SF blends (Papadakis 1999a) are adopted to verify the proposed hydration model. The experimental results including the amount of calcium hydroxide, chemically bound water and porosity are used. The mixing proportions for specimens are shown in Table 2. In the control specimen, the water to cement ratio (W/C) was 0.5 and the aggregate to cement ratio (A/C) was 3. SFA means that silica fume replaces volume of aggregate and SFC means that silica fume replaces volume of cement. The CH content and porosity at 3, 7, 14, 28, 49, 112, 182 and 364 days after casting were tested. The precise measurement of important characteristics for the understanding of the SF activity led to the preparation of the same mixtures but without aggregate.

4.2.1 The amount of calcium hydroxide during the hydration process

In the hydration of ordinary Portland cement, the amount of calcium hydroxide will increase until it reaches a steady state. In the hydration of cement-silica fume blends, the evolution of the amount of CH depends on two factors: such as the Portland cement hydration that produces CH and the

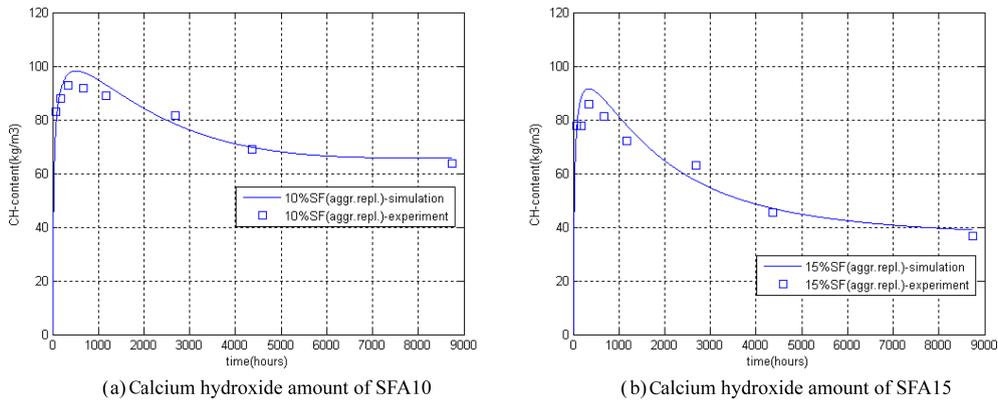


Fig. 6 The comparison between experimental results (Papadakis 1999a) and simulation results of CH amount

pozzolanic reaction that consumes CH. In the initial period the production of CH is the dominant process and then the consumption of CH is the dominant process. In the experiment range (Papadakis 1999a), the CH amount initially increases, reaches a maximum value and then decreases. Based on the amount of calcium hydroxide, the reaction coefficients of the pozzolanic reaction in Eq. (14a) can be obtained (as $k_{rsi}=1.9637E-9$ cm/h, $D_{esi0}=1.4990E-12$ cm²/h). The evolution of the CH amount is shown as a function of the hydration time in Fig. 6. As shown in Fig. 6, the simulation results overall agree well with experimental results.

4.2.2 The mass of chemical bound water and porosity during hydration process

To determine chemical water mass, the specimen was stripped, placed in a preweighted glass mortar and pulverized. The mortar with the material was placed in an oven at 105°C until the weight was constant. These weight indications were used to determine the water content (Papadakis 1999a). As proposed in the hydration model and references (Papadakis 1999a, 1999b), the chemical bound water mainly comes from Portland cement hydration. The pozzolanic reaction between calcium hydroxide and silica fume takes place without additional water binding more than that

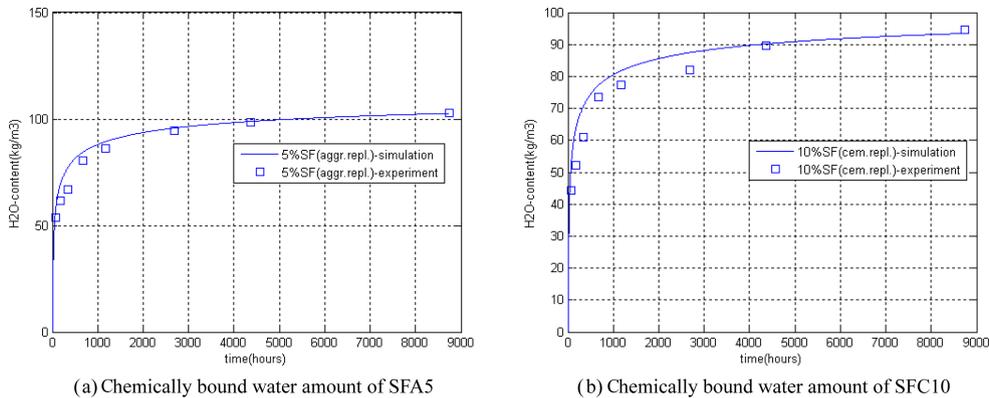


Fig. 7 The comparison between experimental results (Papadakis 1999a) and simulated results of bound water

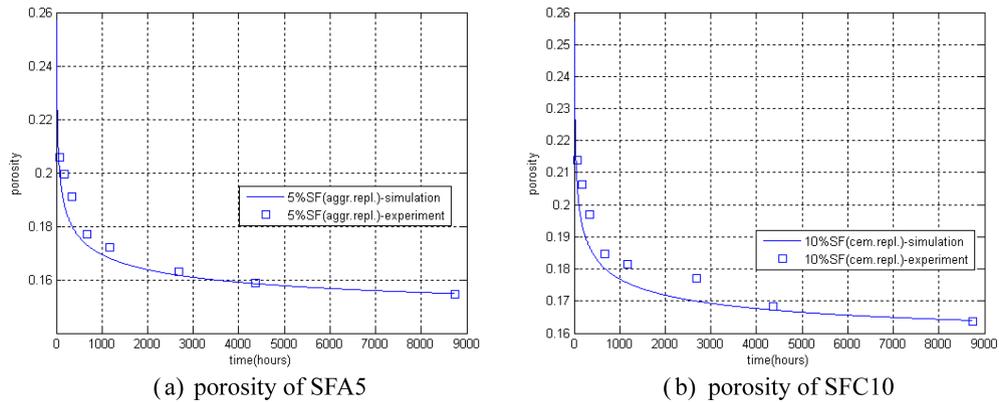


Fig. 8 The comparison between experiment results (Papadakis 1999a) and simulation results of porosity

contained in the CH molecules. The evolution of bound water mass and porosity is shown as a function of hydration time in Figs. 7 and 8 respectively. As shown in Figs. 7 and 8, the simulated results overall agree well with experimental results. The difference between experimental and simulated results is in that the selective reaction of CH with SF instead of its reaction with C_3A and C_4AF phase of cement between 14 days and 6 months, which contributes significantly to water binding (Papadakis 1999a). This selective reaction mechanism is not considered in proposed hydration model. So the simulated result of bound water is a little bigger than experimental result, and the simulated result of porosity is slightly less than experimental result.

5. Modeling of chloride diffusion and reaction in silica fume blended concrete

5.1 Model of chloride diffusion-adsorption in concrete

In most field cases, chloride ion may penetrate into concrete through a combined mechanism of hydraulic advection, capillary suction, diffusion and thermal migration. Diffusion is the dominating mechanism in the case of saturated concrete, such as concrete submerged in seawater. In many papers, chloride transport in concrete is modeled using Fick's second law of diffusion, neglecting the chloride interaction with the solid phase (Mehta 2006). However, several field studies in recent years have indicated that the use of this law is not applicable to long-term chloride transport in concrete, very often calculating a decreasing chloride transport coefficient in time. It is widely accepted that the transport behavior of chloride ions in concrete is a more complex and complicated process than can be described by Fick's law of diffusion. This approach, therefore, can be characterized as semi-empirical, resulting in the calculation of an apparent effective diffusivity.

The binding of chloride ion by cementitious materials is very complicated, and is influenced by many factors including chloride concentration, cement composition, hydroxyl concentration, cation of chloride salt, temperature, supplementary cementing materials, carbonation, sulfate ions and electrical field etc. There is a generally good correlation between C_3A content (or C_4AF when there is lack of C_3A phase) and chloride binding capacity. There is also evidence for the binding of chlorides in CSH gel, possibly in interlayer space. The Na^+ ions can be bound in CSH gel lattice,

especially when the C/S ratio is low (Papadakis 2000). Several secondary chloride-calcium compounds have also been reported. In addition to the chemical binding, the effects of ionic interaction, lagging motion of cations and formation of an electrical double layer on the solid surface all play an important role in the transport of chloride ions in concrete. The relationship between bound and free chlorides is nonlinear and may be expressed by the Langmuir equation, the Freundlich equation, or the modified Brunauer, Emmet and Teller (BET) equation. Of these, the Langmuir equation is both fundamental and easier to use in practical applications (Han 2007, Ishida 2009).

Pereira and Hegedus (1984) were the first to identify and model chloride diffusion and reaction in fully saturated concrete as a Langmuirian equilibrium process coupled with Fickian diffusion. Furthermore, Papadakis *et al.* (1996b) generalized this pioneering model effort of Pereira and Hegedus and extended it to more general conditions, offering an alternative simpler, yet equally accurate, numerical and analytical solution.

Papadakis *et al.* (1996b) proposed that the physicochemical processes of diffusion of Cl^- in the aqueous phase of pores, their adsorption and binding in the solid phase of concrete, and their desorption can be described by a nonlinear partial differential equation for the concentration of Cl^- in the aqueous phase $[Cl^-(aq)]$ (kg/m^3 pore solution). The equations for calculating the Cl^- in the aqueous phase $[Cl^-(aq)]$ and Cl^- bound in the solid phase $[Cl^-(s)]$ (kg/m^3 concrete) are shown as follows

$$\frac{\partial [Cl^-(aq)]}{\partial t} = \frac{D_{e,Cl^-}(1+K_{eq}[Cl^-(aq)])^2}{K_{eq}[Cl^-(s)]_{sat} + \alpha(1+K_{eq}[Cl^-(aq)])^2} \frac{\partial^2 [Cl^-(aq)]}{\partial x^2} \quad (16a)$$

$$[Cl^-(s)] = \frac{K_{eq}[Cl^-(s)]_{sat}[Cl^-(aq)]}{1+K_{eq}[Cl^-(aq)]} \quad (16b)$$

With initial condition: $[Cl^-(aq)] = [Cl^-(aq)]_{in}$ at $t=0$ (initial concentration) and boundary condition: $[Cl^-(aq)] = [Cl^-(aq)]_0$ at $x=0$ (concrete surface) and $(\partial [Cl^-(aq)]/\partial x) = 0$ at $x=M$ (axis of symmetry).

In the Eqs. (16a) and (16b), x is the distance from the concrete surface (m); t is the time (s); D_{e,Cl^-} is the intrinsic effective diffusivity of chloride ion in concrete (m^2/s); K_{eq} is the equilibrium constant for chloride binding (m^3 of pore solution/kg); and $[Cl^-(s)]_{sat}$ is the saturation concentration of chloride ion in the solid phase (kg/m^3 concrete). As observed from Eq. (16b), the chloride binding capacity depends both on $[Cl^-(s)]_{sat}$ (contents of sites that can bind chlorides) and K_{eq} (ratio of adsorption to desorption rate constants).

The intrinsic effective diffusivity of chloride ion in concrete (m^2/s) can be estimated by the following Eqs

$$D_{e,Cl^-} = \frac{2.4 \times 10^{-10}}{\left(\frac{Ce_0 + km_{silica0}}{\rho_c} + \frac{w_0}{\rho_w}\right)^2} (\varepsilon_{eff})^{3.5} \quad (16c)$$

$$\varepsilon_{eff} = \frac{w_0}{\rho_0} - 0.226 \times 10^3 \times (Ce_0 + km_{silica0}) \times \alpha \quad (16d)$$

Where ρ_c is the density of cement, k is the efficiency factor of the silica fume for chloride penetration (based on the fit of experimental results, Papadakis proposed that $k=6$ for silica fume); and ε_{eff} is the effective porosity for diffusion.

Papadakis (2000) determined parameters $[Cl^- (s)]_{sat}$ and K_{eq} from experimental research on chloride binding isotherms. The equilibrium constant for chloride binding was found fairly constant for all mixtures ($K_{eq} = 0.1 \text{ m}^3$ of pore volume/kg Cl^-). And the saturation concentration of chloride in the solid phase can be determined as follows

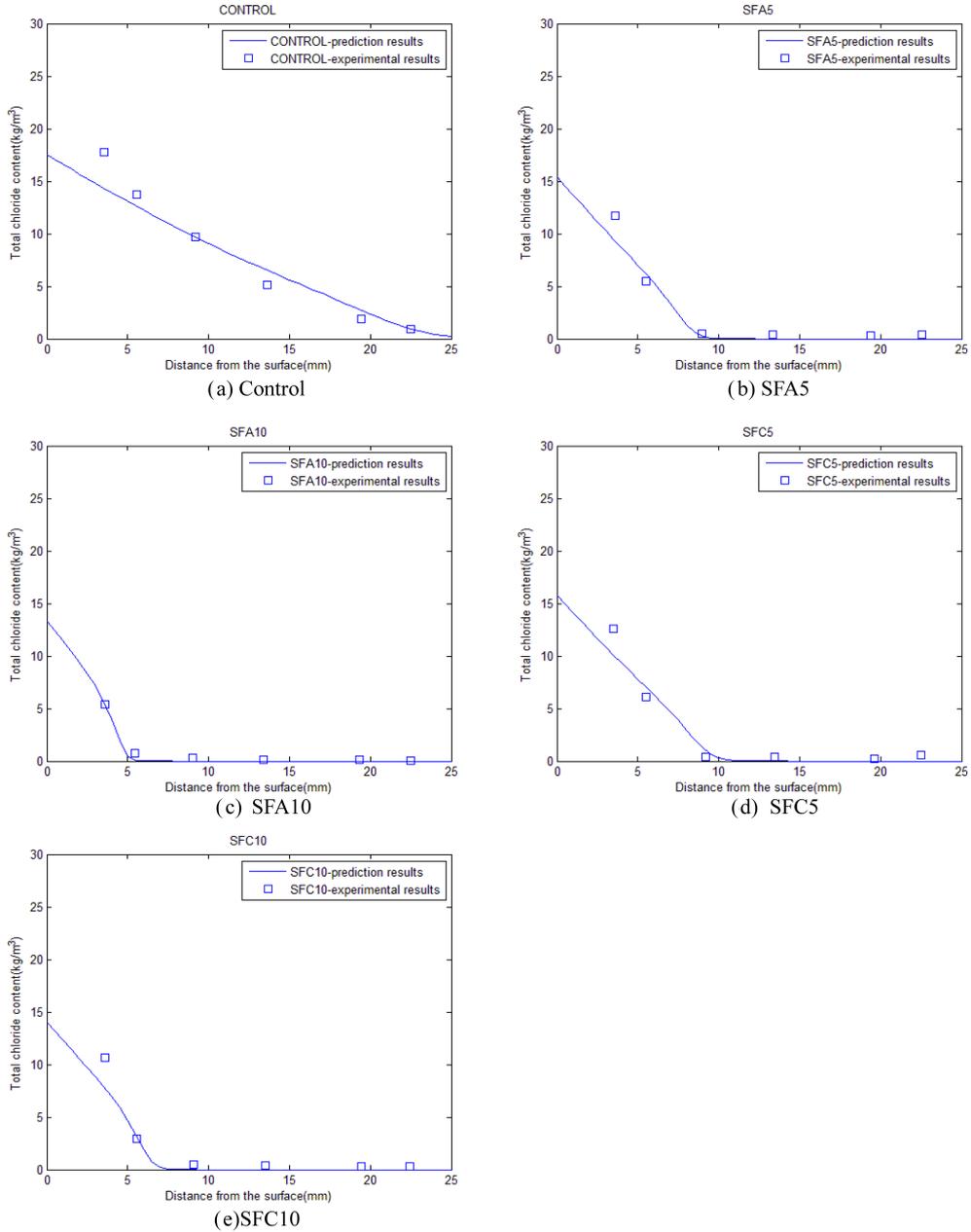


Fig. 9 The comparison between experimental results (Papadakis 2000) and simulated results of chloride penetration profiles

$$[Cl^- (s)]_{sat} = 8.8 \times 10^{-3} \times (C_{e_0} + km_{silica0}) \quad (16e)$$

The Eqs. (16a) and (16b), in space is a boundary-value problem and in time is an initial-value problem. In this paper, a one dimensional finite element method is adopted to solve this equation. For numerical time integration part, the Galerkin method is used to confirm the stability of numerical integration (Logan 2002).

5.2 Verification of the proposed model

Papadakis (2000) made experimental investigations on chloride penetration in silica fume blended concrete according to nordtest method NT Build 443. The mixing proportions of specimens are shown in Table 2. The mortar specimens were cast in steel cylinders of 100 mm diameter and 200 mm height, vibrated for 30 sec on a vibration table, and then hermetically sealed to minimize water evaporation. The molds were stripped after 24 h and the specimens were placed, separately for each mixture, underwater at 20°C for 1 year. For chloride penetration tests, the slice specimen with 60 mm thick was removed from the initially 200 mm specimens. Prior to immersion, the samples were coated with epoxy resin. And then the samples were immersed in a chloride solution (165 g NaCl/L) for 100 days. The temperature was kept constant at 20°C throughout the entire test period. At the end of the immersion period, the exposed surface was ground using a dry process by removing thin successive layers from different depths. The total chloride content of the powders was determined by the Volhard titration method in accordance with the method NT Build code.

By using Eqs. (16a) and (16b), we predicted the total chloride concentration ($\varepsilon[Cl^- (aq)] + [Cl^- (s)]$), as a function of the distance from the outer concrete surface. As shown in Fig. 9, the prediction results generally agree well with the experimental results. The specimens incorporating silica fume, whether it substitutes aggregate of cement, exhibit significantly lower total chloride content for all depths from the surface than the control specimen. Given a certain water to binder ratio, with the increasing of silica fume amount, the ingress depth of chloride ions decreases significantly. On the other hand, depassivation of steel bars takes place when molar concentration of dissolved Cl^- , $[Cl^- (aq)]$, in their vicinity drops below a certain percentage of the molar concentration of hydroxyls in the pore water, $[OH]^-$. The critical value of the $[Cl^- (aq)]/[OH]^-$ ratio which signals depassivation seems to be 0.3 (Papadakis *et al.* 1996b). The molar concentration of $[OH]^-$ depends on the cation type and on whether concrete is carbonated or not. By using the proposed model, we can predict the chloride penetration/binding profiles and estimate the time required for the chloride concentration surrounding the reinforcement to increase over the threshold of depassivation of reinforcing bars. The protection measures against chloride induced depassivation of steel in concrete also can be achieved.

6. Conclusions

In this paper, we proposed a numerical procedure to evaluate the chloride diffusion in silica fume blended concrete. This numerical procedure consists of two sub models, i.e., a hydration model and a chloride diffusion model. First, based on the combination of Papadakis' chemical-based steady-state model and the kinetic reaction mechanisms involved in cement hydration and the pozzolanic reaction, a kinetic model is proposed to describe the hydration process of SF concrete. By

considering the production of calcium hydroxide in cement hydration and its consumption in pozzolanic reaction, the pozzolanic reaction of SF is separated from cement hydration. The proposed model considers the dependence of pozzolanic activity on the mass of calcium hydroxide and the influence of SF on the hydration of Portland cement. The contents of evaporable water, calcium hydroxide, and porosity were obtained as companioned results of the hydration model and were used as input parameters for evaluation of the penetration of chloride ion. Second, in the chloride diffusion model, the physicochemical processes of diffusion of chloride ion in the aqueous phase of pores, the adsorption and binding in the solid phase of concrete, and the desorption are described by a nonlinear partial differential equation. The estimated chloride penetration profiles in the hydrating silica fume blended concrete generally agree with experimental results.

Acknowledgements

This study was supported by the Engineering Research Center designated by the Ministry of Education & Science Technology, the Sustainable Building Research Center, Hanyang University (R11-2005-056-04003). This research was supported by a Project (2010-0014051: study on the carbonation prediction of concrete using Portland blast furnace slag hydration model) from the National Research Foundation of Korea.

References

- Breugel, K. (1995), "Numerical simulation of hydration and microstructural development in hardening cement-based materials (I) theory", *Cement Concrete Res.*, **25**(2), 319-331.
- Han, S.H. (2007), "Influence of diffusion coefficient on chloride ion penetration of concrete structure", *Constr. Build. Mater.*, **21**(2), 370-378.
- Ishida, T., Iqbal, P.O. and Anh, H.T.L. (2009), "Modeling of chloride diffusivity coupled with non-linear binding capacity in sound and cracked concrete", *Cement Concrete Res.*, **39**(10), 913-923.
- Jensen, O.M. and Hansen, P.F. (2001), "Water-entrained cement based materials, I: principles and theoretical background", *Cement Concrete Res.*, **31**(4), 647-654.
- Logan, D.L. (2002), *A first course in the finite element method*, Brooks/Cole Thomson learning, United States.
- Maruyama, I., Suzuki, M. and Sato, R. (2005), "Prediction of temperature in ultra high-strength concrete based on temperature dependent hydration model", *Proceedings of 7th Int. Symp. on High Performance Concrete*, United States.
- Matsushita, T., Hoshino, S., Maruyama, I., Noguchi, T. and Yamada, K. (2007), "Effect of curing temperature and water to cement ratio on hydration of cement compounds", *Proceedings of 12th international congress chemistry of cement*, Montreal.
- Mehta, P.K. (2006), *Concrete-microstructure, properties and materials*, 3rd ed, McGraw-Hill, New York.
- Navi, P. and Pignat, C. (1996), "Simulation of cement hydration and the connectivity of the capillary pore space", *Adv. Cem. Base. Mater.*, **4**(2), 58-67.
- Pane, I. and Hansen, W. (2005), "Investigation of blended cement hydration by isothermal calorimetry and thermal analysis", *Cement Concrete Res.*, **35**(6), 1155-1164.
- Papadakis, V.G. (1999a), "Experimental investigation and theoretical modeling of silica fume activity in concrete", *Cement Concrete Res.*, **29**(1), 79-86.
- Papadakis, V.G. (1999b), "Effect of fly ash on Portland cement systems, Part I: low-calcium fly ash", *Cement Concrete Res.*, **29**(11), 1727-1736.
- Papadakis, V.G. (2000), "Effect of supplementary cementing materials on concrete resistance against carbonation

- and chloride ingress”, *Cement Concrete Res.*, **30**(2), 291-299.
- Papadakis, V.G., Faradis, M.N. and Vayenas, C.G. (1992), “Hydration and carbonation of pozzolanic cements”, *ACI Mater. J.*, **89**(2), 119-130.
- Papadakis, V.G., Faradis, M.N. and Vayenas, C.G. (1996a), “Physicochemical process and mathematical modeling of concrete chlorination”, *Chem. Eng. Sci.*, **51**(4), 505-513.
- Papadakis, V.G., Fardis, M.N. and Vayenas, C.G. (1996b), “Mathematical modeling of chloride effect on concrete durability and protection measures”, *Proceedings of Concrete Repair, Rehabilitation and Protection*, London.
- Park, K.B., Noguchi, T. and Plawsky, J. (2005), “Modeling of hydration reaction using neural network to predict the average properties of cement paste”, *Cement Concrete Res.*, **35**(9), 1676-1684.
- Pereira, C.J. and Hegedus, L.L. (1984), “Diffusion and reaction of chloride ions in porous concrete”, *Proceedings of the 8th International Symposium of Chemical Reaction Engineering*, Edinburgh.
- Saeki, T. and Monteiro, P.J.M. (2005), “A model to predict the amount of calcium hydroxide in concrete containing mineral admixture”, *Cement Concrete Res.*, **35**(10), 1914-1921.
- Song, H.W., Jang, J.C., Saraswathy, V. and Byun, K.J. (2007), “An estimation of the diffusivity of silica fume concrete”, *Build. Environ.*, **42**(3), 1358-1367.
- Tomosawa, F. (1997), “Development of a kinetic model for hydration of cement”, *Proceedings of tenth international congress chemistry of cement*. Gothenburg.
- Yoon, I.S. (2009), “Simple approach to calculate chloride diffusivity of concrete considering carbonation”, *Comput. Concrete*, **6**(1), 1-18.