

## Coupled diffusion of multi-component chemicals in non-saturated concrete

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**Abstract.** A comprehensive simulation model for the transport process of fully coupled moisture and multi-species in non-saturated concrete structures is proposed. The governing equations of moisture and ion diffusion are formulated based on Fick's law and the Nernst-Planck equation, respectively. The governing equations are modified by explicitly including the coupling terms corresponding to the coupled mechanisms. The ionic interaction-induced electrostatic potential is described by electroneutrality condition. The model takes into account the two-way coupled effect of moisture diffusion and ion transport in concrete. The coupling parameters are evaluated based on the available experimental data and incorporated in the governing equations. Differing from previous researches, the material parameters related to moisture diffusion and ion transport in concrete are considered not to be constant numbers and characterized by the material models that account for the concrete mix design parameters and age of concrete. Then, the material models are included in the numerical analysis and the governing equations are solved by using finite element method. The numerical results obtained from the present model agree very well with available test data. Thus, the model can predict satisfactorily the ingress of deicing salts into non-saturated concrete.

**Keywords:** deicing salts; chloride; concrete; coupled effect; Nernst-Planck equation

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### 1. Introduction

Corrosion of reinforcing steel due to chloride attack is one of the major problems for long term durability of reinforced concrete structures. Most of reinforced concrete structures are under non-saturated condition in which chloride ions penetrate into concrete by two driving forces, chloride and moisture gradients. The moisture gradient plays a very important role in the chloride penetration process by carrying chloride ions with the moisture movement (Ababneh *et al.* 2003, Abarr 2005). It is important to note that when the moisture moves in concrete, it carries not only the chloride ions but also many other ions in pore solution. Therefore, to investigate multi-species penetration into concrete, the moisture effect must be considered, and to model the multi-species diffusion process in concrete, the moisture gradient must be incorporated in the governing

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equations. On the other hand, under the non-saturated condition, the moisture movement is also driven by two types of driving forces: the moisture gradient and concentration gradients of the diffusing species which include chloride concentration gradient. In another word, both moisture and ion concentration gradients have strong influence on the ion penetration as well as on the moisture diffusion. The entire transport problem must be considered as a two-way coupling process (Ababneh and Xi 2002, Abarr 2005).

Many researchers have studied the chloride penetration into non-saturated concrete. Saelta *et al.* (1993) developed a numerical model for chloride penetration into partially saturated concrete by considering the effect of the relative humidity on the rate of chloride penetration. They added coupling terms in the governing equations and developed material models for the transport parameters by taking into account the dependence of chloride diffusion on moisture movement and concrete mix parameters. The nonlinear and coupled partial differential equations were solved by using finite element method. Nilsson (2000) proposed a model for chloride penetration into concrete exposed to seawater splash or deicing salt. It was concluded that the chloride diffusion and convection could be described as function of the moisture content in concrete. Miller *et al.* (2004) investigated the chloride ingress into concrete under saturated condition and exposed to cyclic wetting and drying condition. The results showed that the rate of chloride penetration depends on different exposure conditions. For the wetting and drying environment, the chloride penetrates into concrete by sorption and diffusion processes while the diffusion is the dominant mechanism in the saturated concrete. De Vega G. *et al.* (2007) conducted a test for evaluating chloride diffusion coefficients through partially saturated concrete. It was found that the lower the internal humidity in concrete, the lower the chloride diffusion coefficient of concrete. Boulifiza *et al.* (2003) proposed mathematical models and numerical simulations for moisture movement and chloride penetration in concrete based on diffusion and advection mechanisms. The study focused on both cracked and uncracked concrete under saturated and non-saturated conditions. It showed that water movement in a crack is very sensitive to the degree of saturation and the chloride penetration is significantly influenced by existing cracks. Nielsen and Geiker (2003) developed a model, a combination of composite theory and Power's model for microstructural development, to predict the interaction between the chloride diffusion coefficient and degree of saturation in cementitious materials. The study concluded that the chloride diffusion coefficient depends on degree of saturation of concrete.

The systematic study on the coupling effects between chloride penetration and moisture diffusion in concrete was started by Ababneh and Xi (2002) who conducted an experimental study to determine the influence of chloride penetration on moisture diffusion in concrete. The test results showed that the moisture diffusion is significantly affected by chloride penetration. For theoretical modeling, they suggested to use an additional term to take into account the coupling effect in the governing equation for moisture diffusion, while the conventional way is to consider the moisture diffusivity to be dependent of chloride concentration. They also found that the additional term in the governing equation depends linearly on the chloride concentration gradient and the proportional constant is the coupling parameter that can be determined by their testing method (Ababneh and Xi 2002). Three years later, Abarr (2005) developed another testing method to study the effect of moisture diffusion on chloride penetration in concrete. The results showed that the moisture diffusion has significant influence on chloride penetration in concrete. Similar to Ababneh and Xi (2002), they suggested to use an additional term to take into account the coupling effect in the governing equation for chloride penetration, while the conventional way is to consider the chloride diffusivity to be dependent of moisture concentration. They also found that the

additional term in the governing equation depends linearly on the moisture concentration gradient and the proportional constant is the coupling parameter that can be determined by their testing method (Abarr 2005). These two studies showed that chloride penetration and moisture diffusion are two fully coupled diffusion processes in non-saturated concrete, and there are two coupling terms that can be incorporated in the two governing equations for moisture and chloride diffusions, and the two coupling terms can be formulated by using two coupling parameters which are all related to chloride concentration. As a result, the two governing equations are not only fully coupled but also nonlinear.

For multi-species diffusion in concrete, Marchand (2001) proposed the numerical model for cementitious materials subjected to aggressive chemical environments called “STADIUM”. This model was developed based on the set of extended Nernst-Planck/Poisson equations. The model was accounted for the electrical interaction between ions in solution and chemical activity effect. The influence of moisture diffusion was considered in terms of capillary suction. This was performed by incorporating the advection term into governing equations. The governing equations were also modified by taking into account the water content in pore solution. Then, Samson and Marchand (2007) used the STADIUM model to simulate the cement-based materials exposed to pure water and sulfate solution and compared with the test data. Wang *et al.* (2005) developed a mathematical model based on their previous model for simulating electrochemical chloride removal (ECR) process, to predict chloride ions from saline environment to penetrate into concrete. The mathematical model was formulated based on the Nernst-Planck equation and the electrostatic potential was evaluated by an assumption that there is no current flow within concrete pore solution, the nil current. It was found that the ionic interaction and the convection flow of pore solution have significant effect on ionic concentration profiles. Lately, Nguyen *et al.* (2008) proposed a transport model of coupled ion and moisture in porous building materials. The moisture transport was considered in terms of the transport of liquid and vapor phases with aqueous electrolyte theory, and coupled with ion transport in unsaturated porous media. The model was developed based on the Nernst-Planck/electroneutrality set of equations and accounted for the crystallization phenomena on the transport properties. The model was compared with the experimental data obtained by Nuclear Magnetic Resonance (NMR) method. It was shown that the model can be used to simulate the ion transport in plaster/Bentheimer sandstone under various cases with unified ionic diffusivities successfully.

The purpose of this paper is to develop a comprehensive model for the fully coupled process of moisture diffusion and multi-species deicing salts penetration into non-saturated concrete. There are two major improvements from previous diffusion models. The first one is that all governing equations in the present study are two-way coupled, which means that the effect of moisture diffusion on multi-species diffusion will be considered, and the effect of each individual ionic diffusion on moisture movement will also be taken into account. To this end, the formulations of governing equations for multi-ions diffusion in concrete are based on the set of Nernst-Planck/electroneutrality equations, and the Nernst-Planck equation is modified to take into account the effect of moisture diffusion; the governing equation for the moisture diffusion in concrete is based on Fick's law, which is modified to take into account the effect of multi-species diffusions. All coupling effects are expressed explicitly in the governing equations with additional terms representing the coupling mechanisms. The second major improvement is that all material parameters in the governing equations are not simply taken as constants but characterized by material models that incorporate age of concrete and concrete mix design parameters such as aggregate content, water-to-cement ratio and etc. So, the present model can be used for concrete

with various mix designs and ages. The material models for the transport parameters are incorporated in the numerical model, the governing equations are solved by using finite element method, and the numerical results are compared with available test data.

## 2. Basic formulation of governing equations

The flux of each ion transport in an ideal solution in porous media based on the Nernst-Planck equation without considering the chemical activity effects can be described as follow

$$J_i = -D_i \nabla C_i - z_i D_i \left( \frac{F}{RT} \nabla \phi \right) C_i \quad (1)$$

where  $J_i$  is the flux,  $D_i$  is the diffusion coefficient,  $C_i$  is the concentration, and  $z_i$  is the charge number for  $i$ -th diffusing species, respectively;  $F$  is the Faraday's constant,  $R$  is the gas constant,  $T$  is the temperature, and  $\Phi$  is the electrostatic potential; index  $i$  represents  $i$ -th species,  $i = 1, \dots, n$ , and  $n$  is the total number of species considered in the governing equations. As described in Nguyen *et al.* (2006) and Damrongwiriyanupap *et al.* (2010), to simplify the numerical scheme, the electroneutrality condition is selected and incorporated in the model to solve the electrostatic potential which can be expressed as

$$\sum_{i=1}^n C_i z_i = 0 \quad (2)$$

The moisture content in concrete can be expressed by water content ( $w$ ) or by pore relative humidity ( $H$ ). In this study, pore relative humidity is used to represent the moisture content in concrete. Pore relative humidity is considered as a combined indicator of liquid water and water vapor (Bazant and Najjar 1972). The moisture flux ( $J_H$ ) can be described in terms of the gradient of pore relative humidity as follows

$$J_H = -D_H \nabla H \quad (3)$$

in which  $D_H$  is the humidity diffusion coefficient and  $H$  is the pore relative humidity. As described previously, the governing equations, Eqs. (1) and (3), need to be modified in order to take into account the coupling effects. Therefore, the flux of each ion ( $J_i$ ) in non-saturated concrete can be written in terms of free ion concentration gradient and moisture gradient as

$$J_i = -D_i \nabla C_i - z_i D_i \left( \frac{F}{RT} \nabla \phi \right) C_i - D_{i-H} \nabla H \quad (4)$$

in which,  $D_{i-H}$  ((cm<sup>2</sup>mol)/(day l)) is the coupling parameter of the effect of moisture on ionic transport. Similarly, Eq. (3) can be modified by adding the coupling terms for the influence of ionic diffusions on the moisture flux,

$$J_H = - \left( \sum_{i=1}^n D_{H-i} \nabla C_i \right) - D_H \nabla H \quad (5)$$

in which,  $D_{H-i}((\text{cm}^2 \text{ l})/(\text{day mol}))$  are the coupling parameters of the effect of diffusing ions on moisture diffusion, respectively. The mass balance equations of ionic species and moisture can be described as

$$\frac{\partial C_t}{\partial t} = \frac{\partial(C_i + S_i)}{\partial t} = -\nabla J_i \quad (6)$$

$$\frac{\partial w}{\partial t} = -\nabla J_H \quad (7)$$

where  $C_t$  is the total ion concentration which is the summation of free ion ( $C_i$ ) and bound ion concentration ( $S_i$ ); By substituting Eqs. (4) and (5) into, Eqs. (6) and (7), respectively, we obtain

$$\frac{\partial C_t}{\partial t} = \frac{\partial(C_i + S_i)}{\partial t} = \frac{\partial C_t}{\partial C_i} \frac{\partial C_i}{\partial t} = \nabla \left( D_i \nabla C_i + z_i D_i \left( \frac{F}{RT} \nabla \phi \right) C_i + D_{i-H} \nabla H \right) \quad (8)$$

$$\frac{\partial w}{\partial t} = \frac{\partial w}{\partial H} \frac{\partial H}{\partial t} = \nabla \left[ \left( \sum_{i=1}^n D_{H-i} \nabla C_i \right) + D_H \nabla H \right] \quad (9)$$

$(\partial w / \partial H)$  is the moisture capacity; and  $(\partial C_t / \partial C_i)$  is the binding capacity of  $i$ -th ion (will be explained in the next section).

### 3. Material parameters

In order to solve the governing equations, Eqs. (8) and (9), associated with the electroneutrality condition, Eq. (2), the material parameters in the equations must be known. These are the moisture capacity, moisture diffusion coefficient, ionic diffusion coefficients, ionic binding capacities, and the coupling parameters. It is well known that the material parameters depend on mix design and age of concrete and they are not constants. For example, the moisture capacity of concrete depends on aggregate content and microstructure of cement paste, which in turn depends on concrete mix design parameters and age of concrete, and thus in the present study the moisture capacity is characterized by a material model proposed by Xi *et al.* (2000) which takes into account these influential parameters. Similarly, the moisture diffusion coefficient can be described by the composite model taking into account the humidity diffusivity of aggregate and cement paste which can be found in Xi *et al.* (1994b). The chloride diffusion coefficient and chloride binding capacity were discussed in Damrongwiriyanupap *et al.* (2011) which considered concrete mix design parameters. More importantly, in this study, we propose several material models for the coupling parameters based on available experimental results. For reader's convenience, the previously developed transport parameters will be introduced briefly, and then the models for the coupling parameters will be described in detail.

#### 3.1 Moisture Capacity ( $\partial w / \partial H$ )

The moisture capacity of concrete can be determined by the model developed by Xi *et al.* (2000), which is a weight average of the moisture capacities of cement paste and aggregate

$$\frac{dw}{dH} = f_{agg} \left( \frac{dw}{dH} \right)_{agg} + f_{cp} \left( \frac{dw}{dH} \right)_{cp} \quad (10)$$

in which  $f_{agg}$  and  $f_{cp}$  are the weight percentages of the aggregate and cement paste, respectively;  $\left( \frac{dw}{dH} \right)_{agg}$  and  $\left( \frac{dw}{dH} \right)_{cp}$  are the moisture capacities of aggregate and cement paste, respectively, which can be calculated based on the models proposed by Xi *et al.* (1994a, b) and Xi (1995a, b).

### 3.2 Moisture diffusion coefficient ( $D_H$ )

The moisture diffusion coefficient of concrete based on the composite theory derived by Christensen (1979) can be expressed as

$$D_H = D_{H_{cp}} \left( 1 + \frac{g_i}{\frac{[1 - g_i]}{3} + \frac{1}{[(D_{H_{agg}} / D_{H_{cp}}) - 1]}} \right) \quad (11)$$

where  $g_i$  is the aggregate volume fraction,  $D_{H_{cp}}$  is the humidity diffusivity of the cement paste and  $D_{H_{agg}}$  is the humidity diffusivity of the aggregates. According to the fact that the pores in aggregates are discontinuous, the humidity diffusivity of aggregates is very small as compared with the humidity diffusivity of cement paste. Thus,  $D_{H_{agg}}$  in Eq. (11) can be considered negligible. The humidity diffusivity of cement paste can be calculated by the model proposed by Xi *et al.* (1994b).

### 3.3 Chloride diffusion coefficient ( $D_{Cl}$ )

The diffusion coefficient of chloride ions in concrete can be estimated using the multifactor method as follows

$$D_{Cl} = f_1(w/c, t_0) f_2(g_i) f_3(T) f_4(C_f) \quad (12)$$

in which  $f_1(w/c, t_0)$  is a factor accounting for the influence of water-cement ratio ( $w/c$ ) and curing time of concrete ( $t_0$ ). The diffusion coefficient is higher when water-cement ratio increases. A formulation for  $f_1(w/c, t_0)$  was proposed by Xi and Bazant (1999)

$$f_1 = \frac{28 - t_0}{62,500} + \left( \frac{1}{4} + \frac{(28 - t_0)}{300} \right) \left( \frac{w}{c} \right)^{6.55} \quad (13)$$

The second factor,  $f_2(g_i)$ , is incorporated for the effect of composite action of the aggregates and the cement paste on the diffusivity of concrete. This factor can be calculated by using the three

Table 1 Activation energies for various cement paste

w/c	Ordinary portland cement (KJ/mol)	Cement with pozzolans (KJ/mol)
0.4	41.8 ± 4.0	-
0.5	41.8 ± 4.0	4.18
0.6	41.8 ± 4.0	-

phase composite model developed by Christensen (1979)

$$f_2(g_i) = D_{cp} \left( 1 + \frac{g_i}{(1 - g_i)/3 + 1/((D_{agg}/D_{cp}) - 1)} \right) \quad (14)$$

where  $D_{agg}$  and  $D_{cp}$  are the chloride diffusivities of aggregates and cement paste, respectively. These two parameters can be determined by using the model proposed by Martys *et al.* (1994)

$$D = \frac{2(1 - (V_p - V_p^c))}{S^2} (V_p - V_p^c)^{4.2} \quad (15)$$

in which  $V_p$  is the porosity,  $S$  is the surface area, and  $V_p^c$  is the critical porosity (the porosity at which the pore space is first percolated). When Eq. (15) is used for the diffusivity of cement paste,  $D_{cp}$ , then  $V_p$ ,  $S$  and  $V_p^c$  are considered as the parameters for cement paste. The critical porosity may be taken as 3% for cement paste (Martys *et al.* 1994). Based on the study of Xi *et al.* (1994a), the surface areas of cement paste,  $S$ , can be estimated by the monolayer capacity,  $V_m$ , of adsorption isotherm of concrete which is proportional to  $S$ . The porosity,  $V_p$ , can be estimated by adsorption isotherm, at saturation ( $H=1$ ). More detail on adsorption isotherm can be found in Xi *et al.* (1994a, b). The diffusivity of aggregates,  $D_{agg}$ , can be taken as a constant, and a proposed value is  $1 \times 10^{-12}$  cm<sup>2</sup>/s.

The third factor,  $f_3(T)$ , is to consider the effect of temperature on the diffusion coefficient of concrete. This can be calculated by using Arrhenius' law

$$f_3(T) = \exp \left[ \frac{U}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (16)$$

in which  $U$  is the activation energy of the diffusion process,  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  and  $T_0$  are the current and reference temperatures, respectively, in Kelvin ( $T_0 = 296 \text{ K}$ ). According to the studies by Page *et al.* (1981) and Collepardi *et al.* (1972), the activation energy of the diffusion process depends on water-to-cement ratio,  $w/c$ , and cement type which can be found in Table 1.

The fourth factor,  $f_4(C_f)$ , describes the so-called concentration dependence, i.e., the dependence of the chloride diffusion coefficient on the free chloride concentration which can be expressed as follows

$$f_4(C_f) = 1 - k_{ion}(C_f)^m \quad (17)$$

where  $k_{ion}$  and  $m$  are two constants, 8.333 and 0.5, respectively.  $k_{ion}$  and  $m$  were obtained by Xi and Bazant (1999). It should be noted in Eq. (17) and all following equations that  $C_f$  (in grams of chloride per gram of concrete, g/g) is used to represent the free chloride concentration and  $C_i$  is for ionic contractions of all other ions.

### 3.4 Chloride binding capacity ( $\partial C_f / \partial C_t$ )

When chloride ions enter porous concrete, some of them attach to the pore wall (called bound chloride) and some of them diffuse in the pores (called free chloride). The total chloride concentration,  $C_t$ , is the summation of free chloride,  $C_f$ , and bound chloride,  $C_b$ , which can be given by

$$C_t = C_f + C_b \quad (18)$$

The chloride binding capacity is defined as the incremental ratio of the free chloride content and total chloride content

$$\frac{dC_f}{dC_t} = \frac{1}{1 + \frac{dC_b}{dC_f}} \quad (19)$$

The term  $dC_b / dC_f$  can be obtained experimentally. By using the model developed by Xi and Bazant (1999), the chloride binding capacity can be expressed as

$$\frac{dC_f}{dC_t} = \frac{1}{1 + \frac{A10^B \beta_{C-S-H}}{35,450 \beta_{sol}} \left( \frac{C_f}{35.45 \beta_{sol}} \right)^{A-1}} \quad (20)$$

where  $A$  and  $B$  are two material constants related to chloride adsorption and equal to 0.3788 and 1.14, respectively (Tang and Nilsson 1993). The binding capacity depends on the two parameters,  $\beta_{sol}$  and  $\beta_{C-S-H}$ .

The parameter  $\beta_{sol}$  is described as the relationship between the volume of pore solution and weight of concrete (L/g)

$$\beta_{sol} = \frac{V_{sol}}{w_{conc}} = \frac{w_{sol}}{\rho_{sol} w_{conc}} = \frac{n(H, T)}{\rho_{sol}} \quad (21)$$

where  $V_{sol}$  is the volume of pore solution,  $w_{sol}$  is the weight of pore solution,  $w_{conc}$  is the weight of concrete,  $\rho_{sol}$  is the density of the pore solution (g/L) and is dependent on chloride concentration. To simplify the calculation, the parameter  $\rho_{sol}$  can be estimated by using the density of pore water. The weight ratio of pore solution to concrete ( $w_{sol}/w_{conc}$ ) represents chloride adsorption isotherm which is related to relative humidity,  $H$ , temperature,  $T$ , and pore structure of



concrete. Due to a lack of test data on chloride isotherm,  $n(H, T)$  may define as the isotherm of water adsorption instead of chloride isotherm. The adsorption isotherm of concrete can be described in terms of adsorption isotherm of cement paste and aggregate as follows

$$n(H, T) = f_{cp} n_{cp}(H, T) + f_{agg} n_{agg}(H, T) \quad (22)$$

in which  $f_{cp}$  and  $f_{agg}$  are the weight percentages of cement paste and aggregates, and  $n_{cp}(H, T)$  and  $n_{agg}(H, T)$  are the water adsorption isotherms of cement paste and aggregate, respectively.

The parameter  $\beta_{C-S-H}$  can be explained as the weight ratio of C-S-H gel to concrete (g/g). This factor is used to determine the effect of the cement composition and age of concrete on the volume fraction of C-S-H gel which is written as

$$\beta_{C-S-H} = \frac{w_{C-S-H}}{w_{total}} \quad (23)$$

where  $w_{C-S-H}$  and  $w_{total}$  are the weight of C-S-H gel and the total weight of concrete. The details of parameters  $n(H, T)$  and  $\beta_{C-S-H}$  can be found in the paper by Xi (1995a).

The limitation of binding capacity based on the Freundlich isotherm, Eq. (20), is that the term  $\partial C_f / \partial C_t = 0$  when the free chloride concentration,  $C_f$ , is zero because of  $A < 1$ . As a result,  $\partial C_f / \partial C_t = 0$  leads to  $\partial C_f / \partial t = 0$ . This can be concluded that  $C_f$  is a constant at all time steps and equals to initial free chloride concentration. Thus, chloride diffusion never gets to start. To solve this problem, Tang and Nilsson (1993) suggested that the Freundlich isotherm can be used when  $C_f$  is large ( $> 0.01$  mol/l), and the Langmuir isotherm is employed when  $C_f$  is small ( $< 0.05$  mol/l). For these reasons, in the present study, the chloride binding capacity is represented by Langmuir isotherm for initial free chloride concentration ( $C_f = 0$ ), and while the free chloride concentration is more than zero ( $C_f > 0$ ), the chloride binding capacity can be determined by Eq. (20) based on Freundlich isotherm. The Langmuir isotherm is expressed as

$$\frac{1}{C'_b} = \frac{1}{k' C_{bm}} \frac{1}{C'_f} + \frac{1}{C_{bm}} \quad (24)$$

where  $k'$  is an adsorption constant, and  $C_{bm}$  is the bound chloride content at saturated monolayer adsorption (Tang and Nilsson 1993).  $C'_b$  and  $C'_f$  are the bound and free chloride contents used in Eq. (24). The units of these two parameters are in milligrams of bound chloride per gram of calcium silicate hydrate gel (mg/g) and in free chloride per liter of pore solution (mol/l), respectively, which is different from  $C_b$  and  $C_f$ . In the numerical simulation, it is necessary to use the consistent unit. Therefore,  $C'_b$  and  $C'_f$  can be converted and correlated to the unit of  $C_b$  and  $C_f$  as follows

$$C'_b = \frac{1,000 C_b}{\beta_{C-S-H}} \quad (25)$$

$$C'_f = \frac{C_f}{35.45\beta_{sol}} \quad (26)$$

Substituting Eqs. (25) and (26) into Eq. (24), yields

$$\frac{1}{C_b} = \frac{1,000}{\beta_{C-S-H}} \left[ \frac{35.45\beta_{sol}}{k'C_{bm}} \frac{1}{C_f} + \frac{1}{C_{bm}} \right] \quad (27)$$

Eq. (27) can be re-expressed in a simple form as

$$C_b = \frac{1}{\beta + \frac{1}{\alpha C_f}} \quad (28)$$

in which,

$$\alpha = \frac{kC_{bm}\beta_{C-S-H}}{35,450\beta_{sol}} \quad (29)$$

$$\beta = \frac{1,000}{\beta_{C-S-H}C_{bm}} \quad (30)$$

Derivative of Eq. (28) with respect to  $C_f$  yields

$$\frac{dC_b}{dC_f} = \frac{1}{\alpha(C_f)^2 \left( \beta + \frac{1}{\alpha C_f} \right)^2} \quad (31)$$

By substituting Eq. (31) into Eq. (19), the binding capacity based on Langmuir isotherm can be expressed as

$$\frac{dC_f}{dC_t} = \frac{1}{1 + \frac{dC_b}{dC_f}} = \frac{1}{1 + \frac{1}{\alpha \left( \beta C_f + \frac{1}{\alpha} \right)^2}} \quad (32)$$

Eq. (32) is used to calculate the binding capacity when free chloride concentration tends to zero, then the binding capacity is  $1/(1 + \alpha)$ . The parameter  $\alpha$  can be calculated by using Eq. (29) and is dependent on many factors. As a result,  $\alpha$  is definitely a non-zero number. The parameters in chloride binding capacity based on Langmuir isotherm can be obtained from Tang and Nilsson (1993) paper that is  $1/C_{bm} = 0.1849$ ,  $1/(k'C_{bm}) = 0.002438$ ,  $k' = 75.841$  and  $C_{bm} = 5.4083$ .

### 3.5 Coupling parameters ( $D_{i-H}$ and $D_{H-i}$ )

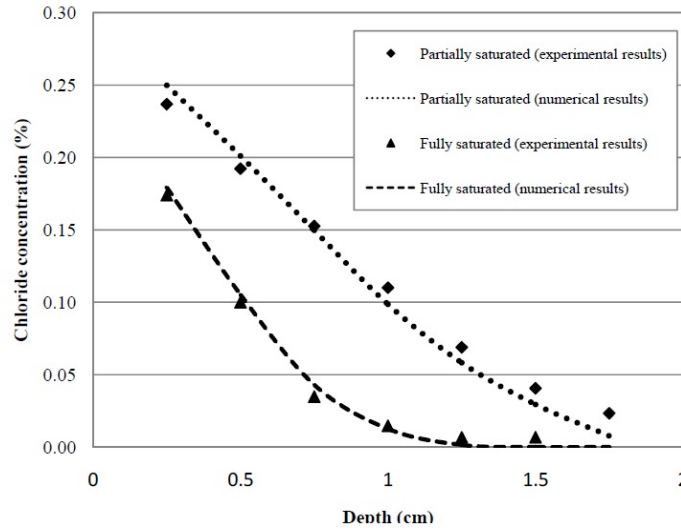


Fig. 1 Comparison of numerical results and experimental results (Abarr 2005) of coupled chloride and moisture diffusion in the non-saturated concrete

So far, there has been no material models developed for the coupling parameters between ion transport and moisture diffusion in concrete,  $D_{H-i}$  and  $D_{i-H}$ . The experimental results of Ababneh and Xi (2002) and Abarr (2005) will be used here to develop models for the coupling parameters. First, Ababneh and Xi (2002) conducted an experimental study to investigate the effect of chloride penetration on moisture diffusion in concrete. The results showed that the coupling parameter,  $D_{H-Cl}$ , is not a constant but depends on chloride concentration. Similarly, Abarr (2005) performed a test to investigate the effect of moisture diffusion on chloride penetration in concrete. The results showed that  $D_{Cl-H}$  increases with increasing chloride concentration and  $D_{Cl-H}$  decreases to zero when the free chloride concentration approaches to zero.

Based on the analyses of test data of Ababneh and Xi (2002) and Abarr (2005), both coupling parameters,  $D_{H-Cl}$  and  $D_{Cl-H}$ , are chloride concentration dependent and they can be expressed in terms of free chloride concentration as follows

$$D_{Cl-H} = \varepsilon C_f \quad (33)$$

$$D_{H-Cl} = \delta C_f \quad (34)$$

in which  $\varepsilon$  and  $\delta$  are two constants depending on concrete mix design. In order to obtain  $\varepsilon$  and  $\delta$ , the results by numerical simulations of coupled chloride and moisture diffusion in concrete are plotted in Fig. 1 and compared with the test data by Abarr (2005). The constants  $\varepsilon$  and  $\delta$  can be obtained by the best curve fitting between numerical and experimental results. In this way,  $\varepsilon$  and  $\delta$  were determined to be  $0.19 \text{ (cm}^2/\text{day)}$  and  $0.52 \text{ ((cm}^2 \text{ l}^2)/(\text{day mol}^2))$ , respectively.

There are no experimental data or material models of coupling parameters for other species,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{OH}^-$  and  $\text{K}^+$ . As the first approximation, the coupling parameters of these ionic species can be evaluated based on the researches for chloride ions (Ababneh and Xi 2002, Abarr 2005). For

example, the effect of moisture on ionic diffusions can be considered as the same constant,  $\varepsilon$ , as used for chloride. This is a reasonable assumption due to the fact that the moisture movement can carry any other ions in the same way as it carries the chloride ions. So, Eq. (33) can be extended to

$$D_{i-H} = \varepsilon C_f = \varepsilon C_i \quad (35)$$

in which the subscript  $i$  represents all ions including chloride.

On the other hand, the effect of ionic diffusion on the moisture diffusion cannot be treated in the same way, that is, the coupling parameter,  $\delta$ , cannot be considered as a constant for all different ions. This is because the effect of the diffusion of a specific ion on the moisture movement varies with the diffusion rate of the ion. As the first approximation, we assume that the ratio of the coupling parameter and the diffusion coefficient of each ion is a constant including chloride,  $D_{H-Cl_f} / D_{Cl} = D_{H-C_i} / D_i$ . This is a reasonable assumption because the effect of an ionic diffusion on the moisture transport is stronger if its own diffusion rate is higher. In this way, the coupling parameter,  $\delta_i$ , of each species can be estimated by the ratio between a specific ionic species and the chloride ion (i.e., the coupling parameter is proportional to the ratio of the diffusion coefficient of the ion and the diffusion coefficient of chloride)

$$\frac{D_i}{D_{Cl}} = \frac{D_{H-C_i}}{D_{H-Cl_f}} = \frac{\delta_i C_i}{\delta C_f} \quad (36)$$

#### 4. Numerical model

Numerical simulations are performed and the governing equations, Eqs. (8) and (9), and electroneutrality condition, can be solved by using the finite element method. The finite element formulation will be briefly introduced here. The continuous variables, ionic species, in the system are spatially discretized over the space domain,  $\Omega$ . The domain discretization can be described as

$$\Omega = \bigcup_{e=1}^{nel} \Omega^e \quad (37)$$

in which  $nel$  is the total number of elements in space domain and  $\Omega_e$  is a subdomain or an element. It is also defined  $\partial\Omega$  as the boundary of space domain and  $\partial\Omega^e$  the boundary of subdomain. By using isoparametric elements, the concentration of each species is defined in terms of nodal values, that is

$$C_i = [N]\{d_i\} \quad (38)$$

where  $[N]$  is the element shape function matrix and  $\{d_i\}$  is the nodal concentration vector of species  $i$ . For the binding capacity of ions, the bound ion concentration is defined as  $S$ . In this study, the binding capacity is considered only for chloride ion so that the release rate of bound chlorides can be described in terms of the ratio of the rates of free and bound chloride concentration,  $\lambda$ , as follows

$$\dot{S}_i = \lambda C_i \quad (39)$$

in which  $\lambda = (\partial C_b / \partial C_f)$  which can be derived following Eq. (31). The nodal free ionic concentrations are solved by substituting Eqs. (38) and (39) into governing equations, Eqs. (8) and (9), and electroneutrality condition expressed as Eq. (2). Then, by applying the Galerkin method to the weak forms of Eqs. (2), (8) and (9), the finite element matrix of transient mass diffusion can be obtained as follows

$$([M_i^S] + [M_i^C])\{\dot{d}_i\} + ([K_i^D] + [K_i^P])\{d_i\} = \{F_i\} \quad (40)$$

in which,

$$[M_i^S] = \int_{\Omega} [N]^T [\lambda_i] [N] d\Omega \quad (41)$$

$$[M_i^C] = \int_{\Omega} [N]^T [N] d\Omega \quad (42)$$

$$[K_i^D] = \int_{\Omega} [B]^T [D_d] [B] d\Omega \quad (43)$$

$$[K_i^P] = \int_{\Omega} [N]^T [D_p] [B] d\Omega \quad (44)$$

( $i$  = number of ionic species = 1, 2, ...,  $n$ )

$\{F_i\} = 0$  which means that no external flux at boundary elements.

## 5. Numerical results and discussions

A concrete slab was used as an example for numerical analysis. The geometry of concrete sample is shown in Fig. 2. It is a 3 cm by 5 cm concrete slab exposed to 0.5 mol/l NaCl and 0.5 mol/l CaCl<sub>2</sub> solutions on the top surface. The ions in concrete pore solution, K<sup>+</sup>, Na<sup>+</sup>, and OH<sup>-</sup>, are also taken into account in the numerical analysis. The material parameters and input data for the numerical simulation are shown in Table 2 including diffusion coefficients, initial concentration at the top surface, and initial concentration in concrete pore solution of each ionic species, water-to-cement ratio, volume fraction of aggregate, and pore relative humidity. The initial relative humidity in the concrete is RH = 50% and the boundary condition on the top surface is RH = 100%. The other boundaries are assumed to be insulated. The specimen is divided into 400 elements and 451 nodes by using isoparametric elements for finite element model.

The profiles of free chloride concentration at different times of exposure are shown in Fig. 3. The depth of chloride penetration is measured from the top surface of concrete sample. It can be seen from the Fig. 3 that the free chloride concentration decreases with increasing depth from the top surface (the initial chloride concentration inside the concrete is zero). At a fixed depth, when the exposure time is longer the free chloride concentration is higher. Fig. 4 shows the distributions

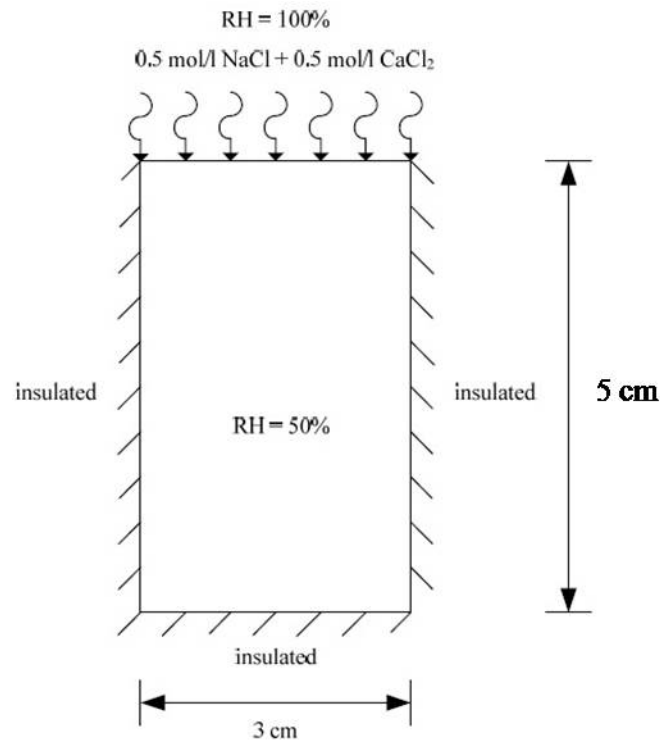


Fig. 2 The concrete sample used in the numerical analysis

Table 2 Material parameters and input data for the concrete sample

Species	K	Na	Cl	OH	Ca
Charge number	+1	+1	-1	-1	+2
Diffusion coefficient, $D_{ci}$	<sup>*</sup> $3.9 \times 10^{-11}$ (m <sup>2</sup> /s)	<sup>*</sup> $2.7 \times 10^{-11}$ (m <sup>2</sup> /s)	$D_{Cl}$ (Eq. 10)	<sup>*</sup> $5.28 \times 10^{-10}$ (m <sup>2</sup> /s)	<sup>§</sup> $2.4 \times 10^{-11}$ (m <sup>2</sup> /s)
Boundary condition at top surface of concrete sample	0	0.5 (mol/l)	1.5 (mol/l)	0	0.5 (mol/l)
Initial condition in pore solution	0.0995 (mol/l)	0.0389 (mol/l)	0	0.1384 (mol/l)	0
Curing time ( $t_0$ )	28 days				
Water-to-cement ratio ( $w/c$ )	0.55				
Volume fraction of aggregate ( $g_i$ )	0.65				
Outside concrete sample	RH = 100%				
Inside concrete sample	RH = 50%				

\* The values are taken from Wang *et al.* (2005).<sup>§</sup>The value is taken from Samson and Marchand (2007).

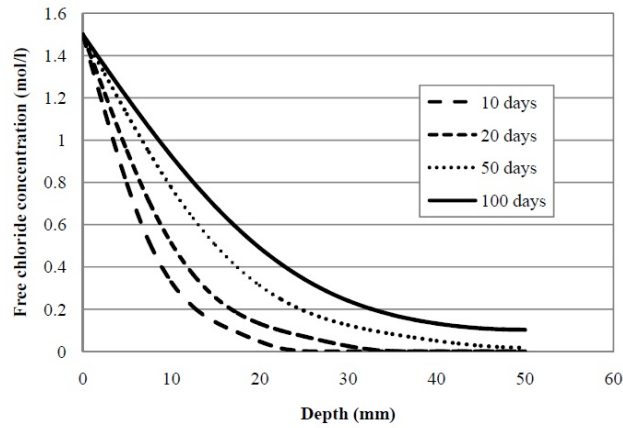


Fig. 3 Chloride profiles at different times of exposure

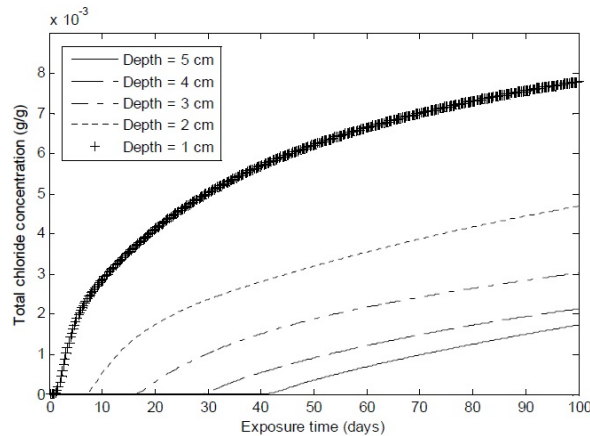


Fig. 4 The total chloride concentration vs. exposure time at different depths

of total chloride with the time of exposure at different depths from the exposed surface. The trends of total chloride concentration are similar to those of free chloride.

The trends of sodium and calcium concentration are similar to free chloride concentration because the boundary and initial conditions for these ions are the same as free chloride. For these three ions, the moisture diffusion and ionic diffusions are in the same direction. This means that the concentrations of chloride, sodium, and calcium are high at the exposed surface and low inside the concrete sample. The profiles of sodium and calcium concentration at different times of exposure are shown in Figs. 5 and 6, respectively.

In contrast to chloride, sodium, and calcium concentration profiles, the concentration of potassium and hydroxyl ions are high inside and low at the exposed surface (there is no sources of potassium and hydroxyl on the top surface). So, the driving forces of concentration gradient for these two ions are in the opposite direction of chloride, sodium, and calcium ions. The profiles of potassium and hydroxyl concentration at different times of exposure are shown in Figs. 7 and 8, respectively. It is noticed from Figs. 7 and 8 that the concentration profiles of potassium and hydroxyl ions are more complicated than those of chloride, sodium, and calcium. They first

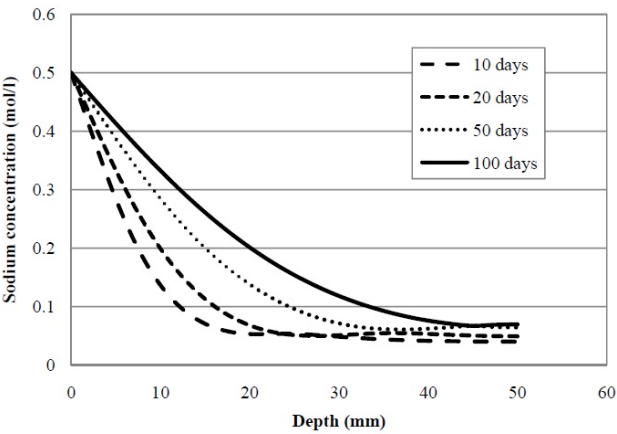


Fig. 5 Sodium profiles at different times of exposure

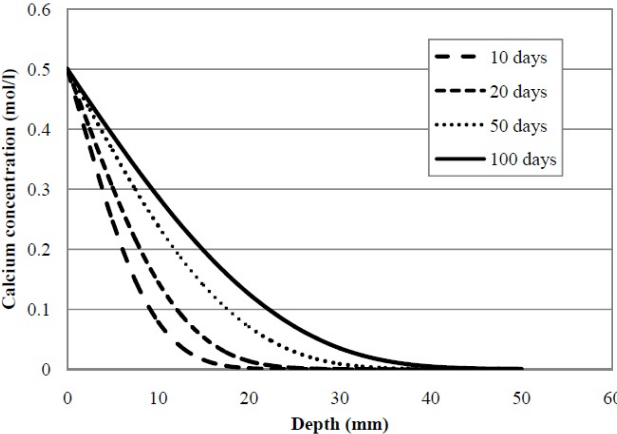


Fig. 6 Calcium profiles at different times of exposure

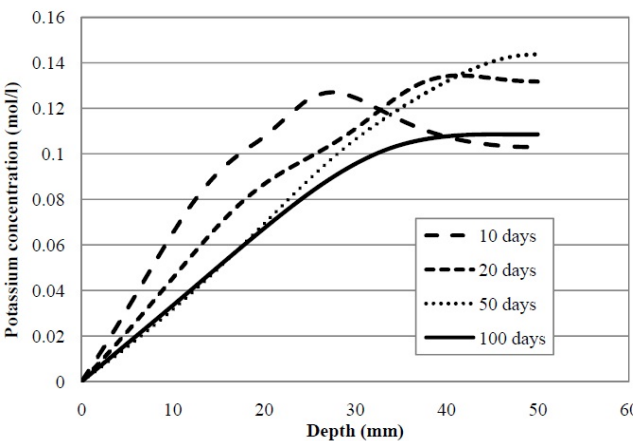


Fig. 7 Potassium profiles at different times of exposure



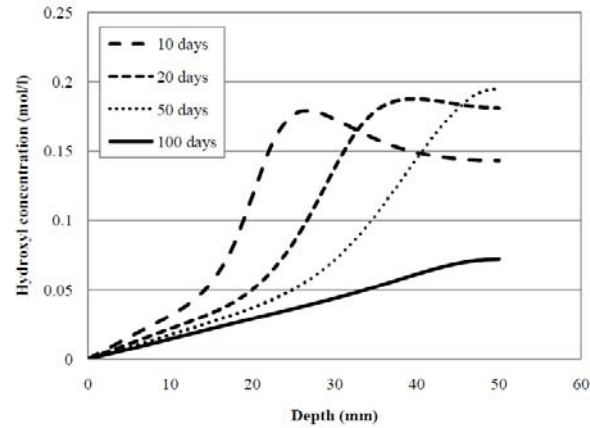


Fig. 8 Hydroxyl profiles at different times of exposure

increase with the increase of depth from the top surface. There are maximum values on the concentration profiles of these two ions at certain depths, which are due to the combined effect of moisture diffusion and electroneutrality condition. As shown in the figures, the depth corresponding to the maximum value increases with increasing exposure time. This is because the effect of moisture gradient increases gradually when the time of exposure increases and it accelerates the penetration rate of chloride, sodium, and calcium ions so that potassium and hydroxyl ions tend to diffuse to a certain depth (i.e., the location of maximum concentration) to satisfy the electroneutrality condition. The maximum value slowly disappears with increasing time, which is shown by the concentration profiles after 100 days of exposure, and this is because the moisture becomes saturated at 100 days which can be seen from the moisture profiles in Fig. 9.

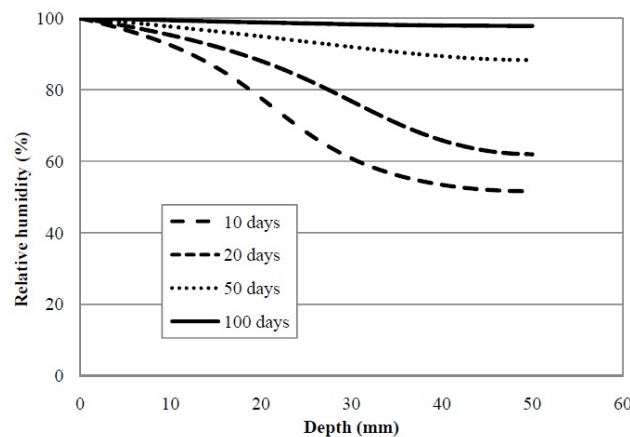


Fig. 9 Moisture profiles at different times of exposure

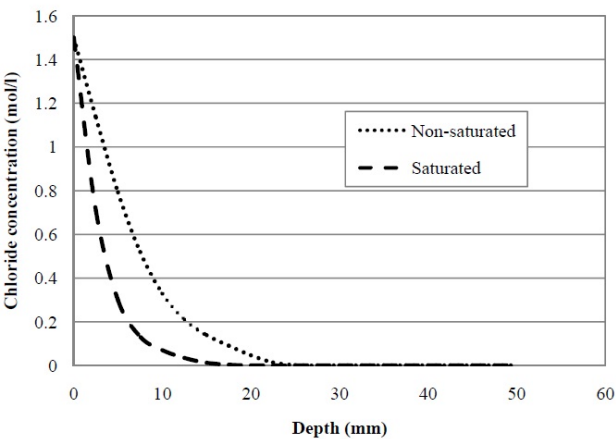


Fig. 10 Chloride profiles at 10 days of exposure under saturated and non-saturated conditions

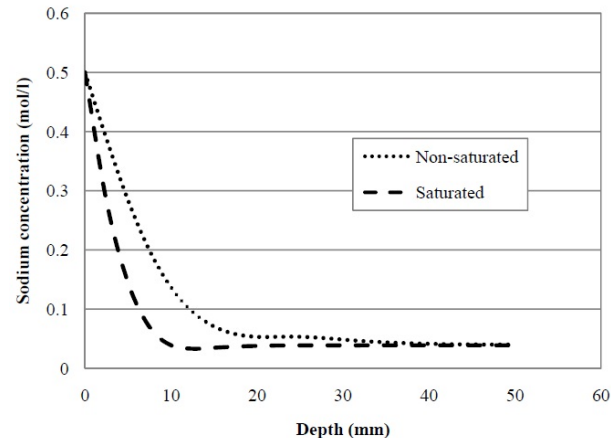


Fig. 11 Sodium profiles at 10 days of exposure under saturated and non-saturated conditions

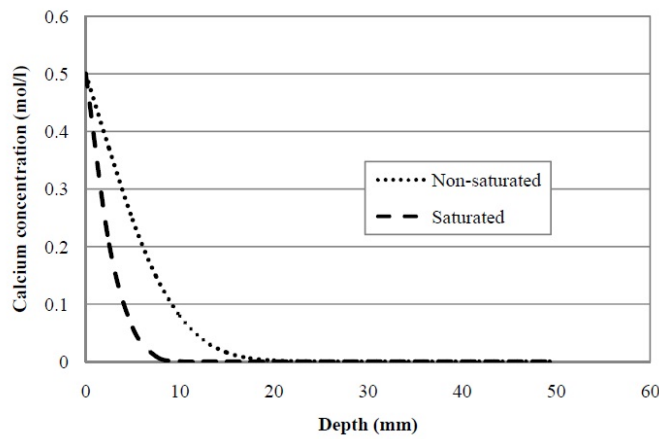


Fig. 12 Calcium profiles at 10 days of exposure under saturated and non-saturated conditions

Fig. 9 shows the moisture profile at 10, 20, 50 and 100 days of exposure. It can be seen from the figures that moisture gradient moves from the exposed surface to inside of concrete specimen. In fact, the moisture gradient is in the same direction of the gradients of chloride, sodium and calcium ions and thus the moisture movement can carry these ions accelerating the penetration rate of these ions.

Figs. 10-14 show the chloride, sodium, calcium, potassium and hydroxyl concentration profiles at 10 days of exposure for non-saturated concrete and saturated concrete. These figures indicate the moisture effect on ionic diffusion in concrete. It is noticed that the moisture condition has significant influence on the diffusion of multi-ionic species in concrete by accelerating the penetration rate of chloride, sodium and calcium. For potassium and hydroxyl ions, their diffusion rates are slowed down by the moisture gradient at the depth close to the exposed surface so that the concentration of these two species is higher in the case of saturated condition than that of non-saturated condition. On the other hand, below this depth, the concentrations of potassium and hydroxyl for non-saturated concrete are higher than saturated condition because of the electroneutrality condition.

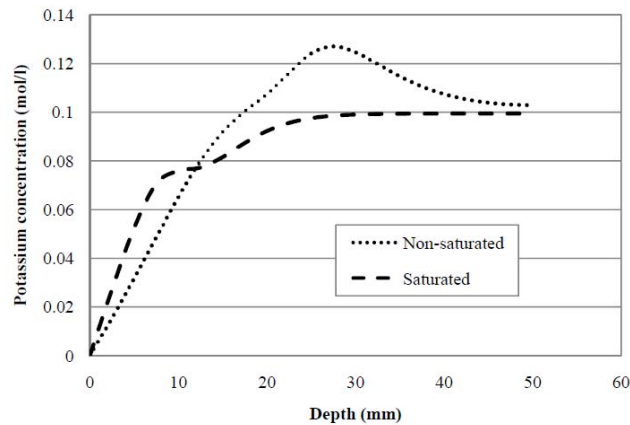


Fig. 13 Potassium profiles at 10 days of exposure under saturated and non-saturated conditions

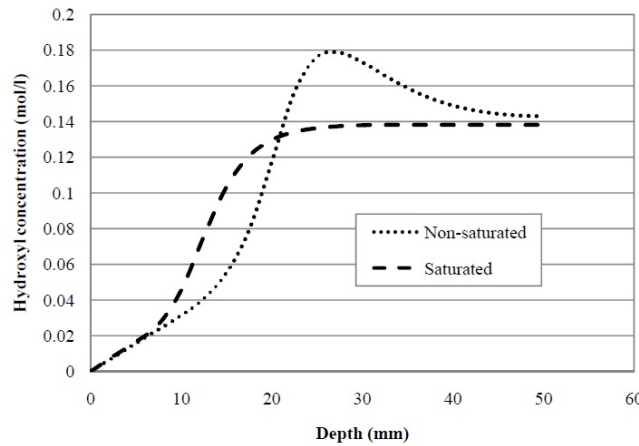


Fig. 14 Hydroxyl profiles at 10 days of exposure under saturated and non-saturated conditions

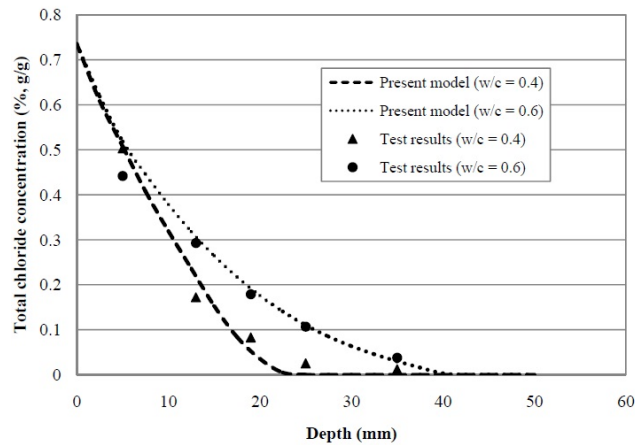


Fig. 15 A comparison between numerical results and test data (Andrade and Whiting 1996)

For the purpose of validation, the present model was used to simulate the test data conducted by Andrade and Whiting (1996). The experimental results are the chloride concentration profiles obtained from the 90-day ponding test of two types of concrete with different water-cement ratios,  $w/c = 0.4$  and  $0.6$ . This was a test of chloride concentration in non-saturated concrete. The concentrations of other ions were not available. A comparison of numerical simulation and test data is shown in Fig. 15. As illustrated, the total chloride concentration predicted by the present model is in very good agreement with the test data. Another comparison is shown in Fig. 1 (Abarr 2005), which shows that the present model can be used for both saturated and non-saturated cases.

## 6. Conclusions

(1) A mathematical model is developed based on the Nernst-Planck equation for multi-ionic diffusion in concrete. The Nernst-Planck equation is modified to simulate the multi-species deicing salts penetration into non-saturated concrete structures by taking into account the moisture effect. Electroneutrality condition is employed to solve for the ionic-induced electrostatic potential. The moisture diffusion in concrete is modeled based on Fick's law, which is modified to take into account the effect of multi-species diffusions.

(2) All governing equations are two-way coupled, that is, the effect of moisture diffusion on multi-species diffusion is considered, and the effect of each individual ionic diffusion on moisture movement is taken into account. All coupling effects are expressed explicitly in the governing equations (the Nernst-Planck equation and Fick's law) with additional terms representing the coupling mechanisms.

(3) The transport parameters related to chloride and moisture diffusion in concrete are not constant but characterized by material models. These models were developed for chloride diffusion coefficient, chloride binding capacity, moisture diffusion coefficient, and moisture capacity. Some of the material models can consider the effect of concrete mix design parameters such as water-to-cement ratio, curing time and type of cement.

(4) The material models for coupling parameters between chloride ions and moisture were developed by using available experimental data. The effect of moisture on all other ions is

assumed to be the same as the effect of moisture on chloride diffusion. This is a reasonable assumption because the moisture transport can carry other ions in the same way as it carries the chloride ions. For the effect of ionic diffusion on moisture transport, we assumed that the ratio of the coupling parameter and the diffusion coefficient of each ion is a constant, including chloride. This is a reasonable assumption because the effect of an ionic diffusion on the moisture transport is stronger if its own diffusion rate is higher. In this way, all coupling parameters can be estimated by the ratio between a specific ionic species and the chloride ion.

(5) The effect of moisture diffusion on ionic diffusion depends on their boundary and initial conditions. Taking the penetration of mixed deicers (e.g. a mixture of NaCl and CaCl<sub>2</sub>) into concrete as an example, the moisture diffusion has significant effect on penetration of deicing salts into concrete by accelerating the penetration rate of chloride, sodium and calcium ions which are in the same direction as the moisture gradient. However, the diffusion of hydroxyl and potassium ions are slowed down by the moisture gradient in a shallow portion of the concrete since the gradients of these two types of ions are in the opposite direction to the moisture gradient. In deep portion of the concrete, the diffusion of hydroxyl and potassium ions are accelerated because of the electroneutrality condition.

(6) The effect of moisture on multi-ion diffusion can be observed by comparing the concentration profiles of chloride, sodium, calcium, potassium and hydroxyl ions in non-saturated and saturated cases. The present example shows that the coupling effect is very significant.

(7) The present model was implemented by the finite element method. To validate the model, the numerical results were compared with an available chloride ponding test of 90-days. It was found that the numerical results agreed very well with the experimental results. Thus, the model can be used to predict satisfactorily the penetration of aggressive chemicals such as deicing salts into non-saturated concrete.

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