Final Report

Coupled Diffusion of Chloride and Other Species in Fly Ash Blended Concrete

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December/ 2016

Contract No. MRG5580222

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Coupled Diffusion of Chloride and Other Species in Fly Ash Blended Concrete

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This project granted by the Thailand Research Fund

บทคัดย่อ

รหัสโครงการ : MRG5580222

ชื่อโครงการ : การแพร่แบบคู่ควบของคลอไรด์และอิออนอื่นๆในคอนกรีตผสมเถ้าลอย

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บทคัดย่อ: คลอไรด์เป็นสารเคมีรุนแรงประเภทหนึ่งที่เป็นภัยคุกคามต่อโครงสร้างคอนกรีตเสริมเหล็ก ซึ่งเป็นสาเหตุทำให้เหล็กเสริมในโครงสร้างคอนกรีตเป็นสนิม ที่ผ่านมาได้มีการนำเสนอแบบจำลองทางคณิตศาสตร์หลายรูปแบบทีเกี่ยวข้องการซึมผ่านของคลอไรด์ในโครงสร้างคอนกรีต ซึ่งสามารถใช้ทำนายเวลาที่เริ่มเกิดสนิมเหล็กในโครงสร้าง แต่อย่างไรก็ตาม แบบจำลองส่วนใหญ่ดังกล่าวไม่ได้พิจารณาถึงคอนกรีตผสมเถ้าลอย ซึ่งจากการศึกษาวิจัยที่ผ่านมาพบว่า เถ้าลอยสามารถช่วยปรับปรุงคุณสมบัติการต้านทานคลอไรด์ของคอนกรีตให้ดีขึ้น ดังนั้นในงานวิจัยนี้จึงมุ่งเน้นพัฒนาแบบจำลองทางทฤษฎีและทางตัวเลขสำหรับคอนกรีตผสมเถ้าลอยที่ต้องเผชิญกับคลอไรด์ในสภาวะไม่อิ่มตัวและอุณหภูมิไม่คงที่ แบบจำลองดังกล่าวสามารถใช้อธิบายการเคลื่อนที่ของอิออนในคอนกรีตผสมเถ้าลอยโดยใช้กฎของฟิกส์และสมการเนิร์สแพงค์ โดยสมการเนิร์สแพลงค์สามารถจำลองกลไกการแพร่เนื่องจากเกรเดียนความเข้มข้นของอิออนและกระบวนการไมเกรชั่นเนื่องจากเกรเดียนความต่างศักย์ไฟฟ้า ซึ่งสามารถใช้ศึกษาการแพร่ของคลอไรด์และอิออนอื่นๆที่อยู่ในสารละลายโพรงคอนกรีตได้แก่ ไฮดรอกซิล โซเดียม โพแทสเซียม และแคลเซียม นอกจากนี้แบบจำลองยังสามารถอธิบายผลกระทบแบบคู่ควบของการแพร่ความชื้นและอุณหภูมิต่อการเคลื่อนที่ของอิออนในคอนกรีต ตัวอย่างทางตัวเลขหลายตัวอย่างซึ่งมีเงื่อนไขความชื้นและอุณหภูมิต่างกันได้ถูกแก้ปัญหาโดยใช้แบบจำลองที่พัฒนาขึ้นมา ผลลัพธ์แสดงให้เห็นว่าความชื้นและอุณหภูมิมีผลกระทบสำคัญต่อการแพร่อิออนในคอนกรีตผสมเถ้าลอย และแบบจำลองดังกล่าวได้ถูกทวนสอบกับผลการทดลอง ซึ่งพบว่ามีความสอดคล้องกันค่อนข้างดี

คำหลัก : คอนกรีต, คลอไรด์, เถ้าลอย, สมการเนิร์สแพลงค์, ผลกระทบคู่ควบ

Abstract

Project Code : MRG5580222

Project Title : Coupled Diffusion of Chloride and Other Species in Fly Ash Blended Concrete

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Project Period : 1 July 2012 – 30 June 2014

Abstract: Chloride is one of the aggressive chemicals that can potentially threaten to reinforced concrete structures. This threat can cause the significant damage due to the corrosion of steel bar. Over the years, there have been several models related to chloride penetration into concrete for predicting the corrosion initiation time of structures. However, most of these models are not considered for concrete containing pozzolanic materials such as fly ash. Since it has been found from several studies, by using fly ash as cement replacement, it can improve chloride resistance. In this study, a theoretical and numerical models were conducted on the ingress of chloride into concrete containing fly ash. The study focused on fly ash concrete subjected to chloride environments under non-saturated and non-isothermal conditions. A theoretical modeling was performed to investigate ion transport in fly ash blended concrete described based on Fick's law and the Nernst-Planck equation. The Nernst-Planck model included diffusion mechanism due to ionic concentration gradient and migration process due to electrostatic potential gradient. The model considered the transport of not only chloride ion but also other chemical species involved in the concrete pore solution such as hydroxyl, sodium, potassium, and calcium ions. The model was extended to study the effect of moisture and temperature on the transport of these ions. The two coupled effects of moisture diffusion and ion penetration; and heat flow and ion diffusion were incorporated in the mathematical model. Several numerical examples were simulated and solved by the proposed model. The results showed that the moisture and temperature had significant effect on ion transport in concrete containing fly ash with various initial and boundary conditions. The proposed model was validated against the test results and a good agreement was observed.

Keywords : Concrete, Chloride, Fly ash, The Nernst-Planck equation, Coupled effect

Executive summary: The penetration of chloride ions into fly ash blended concrete is selected as the focus of this study because it is one of the most difficult diffusion problems encountered in the field of civil engineering. Challenges come from several aspects: diffusing species such as moisture, temperature, chloride, and other ions in concrete pore solution, Na^+, K^+, and OH^-, are coupled among themselves, the porous media (i.e. concrete) is heterogeneous at both large and small scale levels, the internal structure of fly ash concrete is different from those of regular concrete, and the environmental conditions are highly random. On the other hand, development of reliable solutions of the problem has very significant economic impact to the general public. This is because chloride-induced corrosion of reinforcing steel is one of the most severe problems for long term durability of concrete structures. Since chloride penetration plays an important role in determining the service life of reinforced concrete structures, it is necessary to develop theoretical and/or numerical model that can accurately predict the chloride penetration mechanism. This means to consider as much as possible the influencing factors such as moisture and temperature condition, the ionic interaction among chloride and other ions in concrete pore solution, and internal structure that can affect the transport property of fly ash blended concrete.

In saturated concrete and isothermal condition, chloride ions ingress into concrete mainly due to chloride concentration gradient. In this case, there is no movement of moisture and temperature that influence on the chloride penetration process. On the other hand, in non-saturated concrete, other mechanisms involve in the chloride transport mechanism. Moisture transport greatly affects chloride penetration by carrying chloride ions similar to moisture which is influenced by chloride transport process. For non-isothermal condition, by increasing temperature, it can increase the rate of chloride ingress into concrete. Temperature variation also has the effect on moisture diffusion that, for example, moisture transport in masonry walls is affected by heat flow. As the actual condition of reinforced concrete structures exposed to chloride environments is most likely in non-saturated and non-isothermal conditions, thus, the diffusion process of chloride ions in non-saturated and non-isothermal concrete must consider other transport mechanisms such as moisture and heat flow. In this project, we derived the governing equations for the chloride diffusion based on Fick's law and the Nernst-Planck equation taken into account the condition of saturated, non-saturated and non-isothermal fly ash blended concrete. For the latter two conditions, moisture transport and heat flow must be included in the mathematical model.

Fly ash has been widely used as a mineral admixture in normal and high strength concrete. Hydration of concrete containing fly ash is much more complex than those of regular concrete because of the pozzolanic reaction in an aluminosilicate glass phase in fly ash. The products of this reaction can affect the internal structure which is related to the transport property of concrete. Consequently, the other two challenges of this study are to incorporate the kinetic model of hydration activity and

pozzolanic reaction of fly ash in the material model for multi-species diffusion and to characterize the internal structure of fly ash blended concrete.

In this study, the finite element method is employed to solve the mathematical model of coupled partial differential equations of moisture, temperature, and multi-ionic species diffusion in fly ash blended concrete based on Fick’s law and the Nernst-Planck equation. Several numerical examples were simulated and solved by the proposed model. The results showed that the moisture and temperature had significant effect on ion transport in concrete containing fly ash with various initial and boundary conditions. The proposed model was validated against the test results and a good agreement was observed. The prediction models developed in the present study will be useful for long-term durability design and evaluation of reinforced concrete structures containing fly ash.

1 Introduction to the research problem and its significance

There are many practical problems in civil engineering and structural engineering that can be mathematically characterized by diffusion equations of different degrees of complexity. Penetration of chloride ions in concrete structures is a typical example. Other important examples are heat conduction in steel and concrete structures under fire, which is one of the causes for the collapse of the two towers of World Trade Center; and water penetration into the levee in New Orleans which attributed to the failure of the levee when Katrina struck. The penetration of chloride ions into fly ash blended concrete is selected as the focus of this study because it is one of the most difficult diffusion problems encountered in the field of civil engineering. Challenges come from several aspects: diffusing species such as moisture, temperature, chloride, and other ions in concrete pore solution, Na^+, K^+, and OH^-, are coupled among themselves, the porous media (i.e. concrete) is heterogeneous at both large and small scale levels, the internal structure of fly ash concrete is different from those of regular concrete, and the environmental conditions are highly random. On the other hand, development of reliable solutions of the problem has very significant economic impact to the general public. This is because chloride-induced corrosion of reinforcing steel is one of the most severe problems for long term durability of concrete structures. For example, marine concrete structures in splash and tidal zones are often exposed to chloride environments. In such condition, concrete is susceptible to the chloride penetration which induces corrosion of reinforcement. If chloride concentration at the level of reinforcing rebar reaches a critical value, the corrosion process starts and eventually causes the deterioration of reinforced concrete structures. This is a serious problem in concrete industry and greatly affects the service life of reinforced concrete structures. In addition to reducing the cross-section area of rebar itself, it eventually causes the spalling and delamination of concrete cover. All of these damages lead to reduce load bearing capacity and aesthetic aspect which must require repair and/or rehabilitation. Since chloride penetration plays an important role in determining the service life of reinforced concrete structures, it is necessary to develop theoretical and/or numerical model that can accurately predict the chloride penetration mechanism. This means to consider as much as possible the influencing factors such as moisture and temperature condition, the ionic interaction among chloride and other ions in concrete pore solution, and internal structure that can affect the transport property of fly ash blended concrete.

In saturated concrete and isothermal condition, chloride ions ingress into concrete mainly due to chloride concentration gradient. In this case, there is no movement of moisture and temperature that influence on the chloride penetration process. On the other hand, in non-saturated concrete, other mechanisms involve in the chloride transport mechanism. Moisture transport greatly affects chloride penetration by carrying chloride ions similar to moisture which is influenced by chloride transport process (Ababneh and Xi 2002 and Abarr 2005). For non-isothermal condition, by increasing temperature, it can increase the rate of chloride ingress into concrete (Isteita 2009). Temperature variation also has the effect on moisture diffusion which is observed from the study by Khoshbakht et al. (2009) that moisture transport in masonry walls is affected by heat flow. As the actual condition of reinforced concrete structures exposed to chloride environments is most likely in non-saturated and non-isothermal conditions, thus, the diffusion process of chloride ions in non-saturated and non-isothermal concrete must consider other transport mechanisms such as moisture and heat flow. In this project, we will derive the governing equations for the chloride diffusion based on the condition of saturated, non-saturated and non-isothermal fly ash blended concrete. For the latter two conditions, moisture transport and heat flow must be included in the mathematical model.

Fly ash has been widely used as a mineral admixture in normal and high strength concrete. Hydration of concrete containing fly ash is much more complex than those of regular concrete because of the pozzolanic reaction in an aluminosilicate glass phase in fly ash. The silicate in this phase is proposed to react with calcium hydroxide ($Ca(OH)_2$), the product of cement hydration, and produces calcium silicate hydrate (C-S-H) without additional water binding (Wang et al. 2009). Based on the hydration activity and pozzolanic reaction, there are amount of three major hydration products changing during hydration period such as calcium hydroxide ($Ca(OH)_2$), calcium silicate hydrate (C-S-H), and chemically-bound water. These products can affect the internal structure which is related to the transport property of concrete. Consequently, the other two challenges of this study are to incorporate the kinetic model of hydration activity and pozzolanic reaction of fly ash in the material model for multi-species diffusion and to characterize the internal structure of fly ash blended concrete.

In this study, the finite element method is employed to solve the mathematical model of coupled partial differential equations of moisture, temperature, and multi-ionic species diffusion in fly ash blended concrete based on the Nernst-Planck equation. The prediction models to be developed in the present study will be useful for long-term durability design and evaluation of reinforced concrete structures containing fly ash. On the other hand, the prediction model can also be used in practice for by management agency of infrastructure systems.

The motivations of this project are to characterize the internal structures related to transport property of fly ash blended concrete, study diffusion mechanisms of coupled chloride and other chemical species in concrete pore solution, Na^+, K^+, and OH^-, in saturated, non-saturated and non-isothermal condition, and to develop reliable prediction models for the diffusion processes of chloride which can be used to estimate the corrosion initiation time of embedded steels in concrete structures containing fly ash.

1.1 Objectives

The purpose of the proposed research is to develop a novel computational model able to provide accurate long-term prediction for multi-ionic components, moisture, and heat transport in fly ash blended concrete structures.

The specific objectives of the proposed project are

- Establish a complete set of governing equations for the multi-components transport processes in fly ash blended concrete. These equations will be based on the existing physical models, Fick's law and the Nernst-Planck equation. One major improvement will be incorporation of the coupling effects between the ions, and between ions and the pore surfaces. Some parameters incorporated in the governing equations for multi-species diffusion in conventional concrete will be modified for fly ash blended concrete such as chloride diffusivity and chloride binding capacity. Another major improvement will be the extension of the model to non-saturated and non-isothermal concrete containing fly ash, i.e. the moisture and heat transport equations will be incorporated.
- Develop multi-scale models for the material parameters involved in the governing equations. The effective material parameters at meso-scale will be determined based on the constituent phases of the microstructure of fly ash blended concrete.
- Develop the coupling parameters accounted for the coupled effects among multi-ions, moisture, and heat transport in the non-saturated and non-isothermal concrete containing fly ash. Theses parameters will be evaluated based on the experimental studies and included in the governing equations.
- Develop numerical algorithms for solving the stochastic transport equations in which the material parameters, initial condition, and boundary conditions are random. The finite element simulation techniques will be employed to analyse the coupled penetration of chloride and other species in fly ash blended concrete structures.

2 Literature review

Several theoretical and analytical models proposed in the published literatures have been adopted to study the transport mechanism of multi-species in concrete structures, the characterization of the internal structure of concretes, and hydration model of fly ash blended concrete. The diffusion models will be further developed to take into account the effect of fly ash on transport property, and chloride and ion penetration in fly ash blended concrete. The reviews can be grouped here into three categories as following:

2.1 Governing equations for multi-ionic components transport processes

The process of reinforcement corrosion is normally divided into an initiation period during which chlorides are penetrating into the concrete and initiating the corrosion; and a propagation period during which the reinforcement is actively corroding. The initiation period is much longer than the propagation period, because once the corrosion starts, it will take only a few years to crack the concrete cover. Therefore, improving the penetration resistance of concrete to various chlorides is a challenging task in concrete and construction industries, and equally important is to predict the chloride penetration into concrete structures by mathematical models, which provide critical information for structure owners and management agencies. There are two types of the mathematical models, (i) phenomenological models based on a simple solution of one-dimensional diffusion equation (Thomas and Jones, 1996; Boddy et al, 1999); and (ii) physical models based on sophisticated transport theories. Both types of models require information about boundary and initial conditions and test (or monitoring) data to validate the predictions. These data usually consist of measured chloride penetration profiles obtained from structures in service or from laboratory specimens. Chloride penetration in concrete is a long-term process during which not only environmental conditions but also the characteristics of concrete materials vary significantly. This is why reliable data are scarce, which makes it difficult to quantitatively verify the mathematical models.

The phenomenological models are based on the assumption that the process of chloride ions ingress into concrete is a “diffusion” process which follows Fick’s second law,

$$\frac{\partial C(x,t)}{\partial t} = D_a \frac{\partial^2 C(x,t)}{\partial x^2} \tag{1}$$

where *x* is the depth coordinate measured from the concrete surface, *t* is the time, *C(x,t)* is the chloride concentration at depth *x* and time *t*, D_a is the apparent diffusion coefficient. If D_a is a constant, one can solve equation (1) for the condition of constant surface chloride and a one-dimensional infinite depth, the solution is,

$$C(x,t) = C_o(1 - erf\frac{x}{2\sqrt{D_a t}}) \tag{2}$$

where C_o is the surface chloride concentration and *erf(.)* is the error function. If the surface chloride concentration, apparent diffusion coefficient and position of the reinforcement are known then the chloride concentration at the reinforcement level at any time can be predicted using equation (2).

The main problem of the phenomenological models is that the apparent diffusion coefficient D_a is not a constant, it varies by more than one order of magnitude and depends on many factors (Vu and Stewart 2000; Daigle et al., 2004). If the variations of initial and boundary conditions were to be taken into account the prediction error of equation (2) could be even larger. To solve this problem, some physical models have been developed based on transport theories of ionic species in porous media (Li and Page 1998; 2000; Snyder and Marchand 2001, Wang et al., 2005). This type of models considers the transport of not only Cl^- ions but also other chemical species involved in the concrete pore solution such as OH^-, Na^+, and K^+ ions. The transport process involves diffusion due to ionic concentration gradient, migration due to electrostatic potential gradient and convection due to hydrostatic pressure gradient. Mathematically, this can be expressed as,

$$\tau^2 \frac{\partial C_k}{\partial t} = \frac{\partial}{\partial x}(D_k \frac{\partial C_k}{\partial x} + z_k D_k \frac{F}{RT}\frac{\partial \phi}{\partial x} C_k - v\tau C_k) \qquad (k = 1, 2, \ldots) \qquad (3)$$

where τ is the tortuosity of concrete pore structure, C_k is the concentration, D_k is the diffusion coefficient, z_k is the charge number, F is the Faraday's constant, R is the gas constant, T is the temperature, $\varnothing$ is the electrostatic potential, v is the velocity of bulk solution, and index k stands for the k-th species. The electrostatic potential can be determined based on three different methods. Samson and Marchand (2007) selected Poisson's equation to solve the electrostatic potential for ion transport in cement-based materials described as Eq. (4). The advantage of Poisson's equation is that it can be applied in more general cases (Samson et al. 1999). The nil current assumption was used by Li and Page (2000), Wang et al. (2001), and Wang et al. (2005). This method is based on the fact that there is no net current flow within the concrete pore solution, which is described by Eq. (5). Different from those researchers, in this study, the electroneutrality approach is used to determine the electrostatic potential, which can be expressed by Eq. (6). The electroneutrality condition is based on the fact that the charges from all ions exist in the solution must be balanced out as zero.

$$\nabla^2 \phi + \frac{F\left(\sum z_i C_i + w\right)}{\varepsilon} = 0 \qquad (4)$$

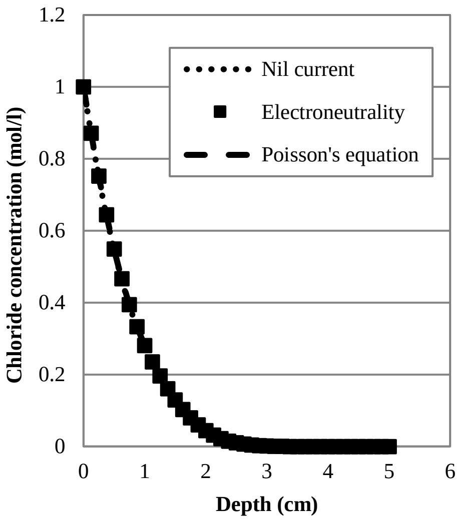
$$I = F\sum_{i=1}^{n} z_i J_i \qquad (5)$$

$$\sum_{i=1}^{n} C_i z_i = 0 \qquad (6)$$

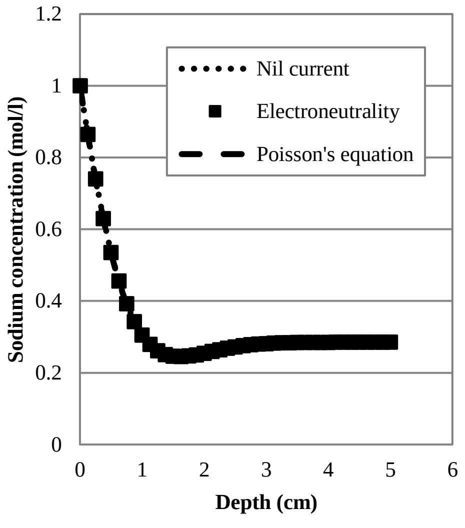
in which w is the fixed charge density, ε is the dielectric constant of the surrounding medium, and I is the external current density.

A study was conducted by Nguyen et al. (2006) and Damrongwiriyanupap (2010) to compare among nil current, Poisson's equation, and electroneutrality condition in modeling of chloride penetration into concrete. The study showed a good agreement of concentration profiles of chloride and other ions obtained by using the three different methods. Based on the mentioned comparative studies, the electroneutrality method is used in the present study. One of the advantages of using electroneutrality condition rather than Poisson's equation is the simplicity of the governing equations, which can significantly reduce the computation time. More importantly, a difficulty in computational schemes associated with the Poisson's equation can be avoided. As shown in Eq. (4), $F/\varepsilon \approx 10^{16}$, which is a very large number often causing numerical difficulty in the computation (Nguyen et al. 2006 and Wang et al. 2005). Fig. 1 shows the comparative study in solving the electrostatic potential of multi-ionic species diffusion in concrete by using three different approaches (Damrongwiriyanupap 2010).

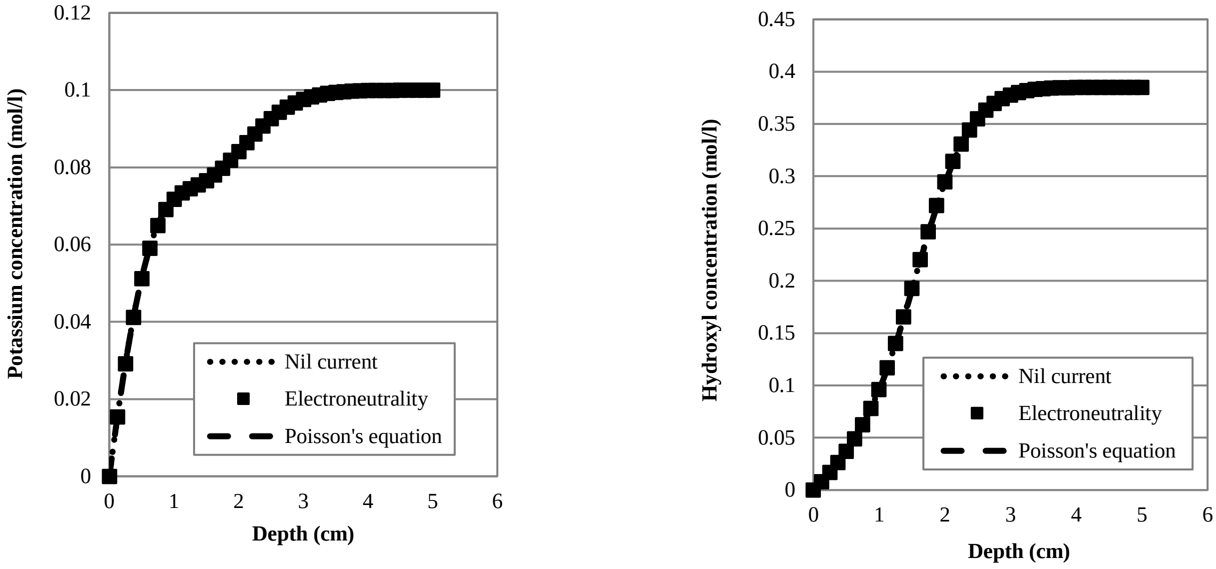
Equations (3) and (6) provide a basic framework for modelling the transport of ionic species in a saturated porous medium from which the concentrations of each individual species present in the electrolyte can be determined if the initial and boundary conditions are defined. In contrast to the empirical models, the physical models include the interactions between different chemical species and thus, the diffusion coefficients in the physical models are defined to each individual species and therefore they have less variability.



(a) Cl^-



(b) Na^+



c) K^+ d) OH^-

Fig. 1 Concentration profiles of four ionic species obtained by the three different approaches

2.2 Multi-scale approaches for modelling the material parameters

A reinforced concrete structure can be observed at multiple scale levels, including macro-scale, meso-scale, and micro-scale. For the transport problem, the governing equations are usually established at the meso-scale level. Therefore, the material parameters in the governing equations are effective material properties at the meso-scale (the so-called representative volume element, RVE). In general, the effective material parameters of RVE are not constants, but complicated functions related to physical and chemical characteristics of the microstructure. Theoretical models need to be developed to complete the connection between the effective material parameters at the meso-scale and the physical and chemical characteristics at the micro-scale. On the other hand, finite element methods are commonly used to complete the connection between the macrostructure and mesostructure.

Meso-scale structure of concrete is composed of gravels, sands, and cement paste (which glue all components together). We usually do not consider the gravels and sands any further in the multi-scale approach, because the gravels and sand particles have higher resistance to the transport processes than that of the cement paste. Moisture and various ions penetrate concrete mainly through cement paste not gravels and sands. Micro-scale structure for cement paste is composed of various hydration products and pores. The resistance of the microstructure to the moisture and ionic transport processes depends on spatial distribution of the hydration products, pore volume, pore size distribution, and pore connectivity. There have been no comprehensive multi-scale models available for characterizing the transport properties of fly ash blended concrete.

2.3 Hydration activity model of fly ash blended concrete

As mentioned before, the hydration activity in fly ash blended concrete is much more complicated than those of regular concrete. This is because the chemical composition in fly ash such as the silicate in aluminosilicate glass phase can react with $Ca(OH)_2$, produced from hydration product of cement, and form calcium silicate hydrate (C-S-H) which is one of the major constituents of cement paste. In another word, during the hydration process and pozzolanic reaction, the amount of $Ca(OH)_2$ decreases which is consumed by aluminosilicate glass phase in fly ash and this chemical reaction is corresponding to produce additional C-S-H. As a result, there is the change in the amount of $Ca(OH)_2$ and C-S-H that can affect the characteristic of cement paste microstructure leading to the change of transport property of concrete. There have been several studies to investigate the hydration reaction of fly ash blended cement paste or concrete which will be discussed as following:

Papadakis (1999) proposed the analytical model to study the hydration mechanism of cement containing low-calcium fly ash. This study investigated the development of strength, heat, bound water, and calcium hydroxide content during hydration period. Fly ash was used to replace aggregate and cement. The higher strength was found after 14 days in aggregate replacement whereas, in cement replacement, strength gained after 91 days. The increasing of strength was found to be roughly proportional to the content of active silica in concrete volume. It was observed from the results of bound water and porosity that when fly ash reacted with calcium hydroxide it produced small amount of bound water. The estimation of the chemical and volumetric composition of fly ash concrete can be calculated by using the reaction stoichiometry. The quantitative expressions from this model can be used to predict the concrete performance in any mix designs. Then, Papadakis (2000) extended the study to investigate cement performance containing high calcium fly ash. The results showed that the mixtures with aggregate replaced by fly ash had higher strengths, higher water binding, and low porosity from the beginning of hydration whereas, in the case of cement replacement, the strength remained constant. The study presented the simplified scheme describing the chemical reactions of high calcium fly ash in hydrating cement paste and developed the mathematical expressions to calculate the reaction products and porosity. Saeki and Monteiro (2005) conducted the experimental study to investigate the degree of reactivity of fly ash and blast furnace slag in concrete. The results showed that the chemical reaction between calcium hydroxide and mineral admixtures (i.e. fly ash) depended on the amount of calcium hydroxide and the degree of hydration of fly ash. The mathematical model was formulated based on the experimental results to predict the reaction between calcium hydroxide and fly ash during hydration period. The model was validated by the test results of cement mortar specimens. The results from the present model had a good agreement with test results. The parameters of this prediction model were related to the physical and chemical compositions of fly ash. Wang et al. (2009) developed the kinetic hydration model based on a multi-component basis. This model was used to simulate hydration of cement paste containing low calcium fly ash. The cement hydration and pozzolanic reaction took into account cement paste mixtures. The time-dependent activity of hydration such as reaction ratio of fly ash, calcium hydroxide content, heat evolution, porosity, chemically bound water, and strength development of fly ash cement paste can be predicted by using the proposed model. The numerical results from the model agreed well with experimental results. Then, Wang and Lee (2011) further developed the numerical model of hydration activity for concrete incorporating fly ash or slag. The model was employed to calculate the amount of calcium hydroxide and its consumption during cement hydration and pozzolanic activity. The heat rate evolution of concrete containing fly ash or slag can be calculated by this model. The model verification was performed by comparing the numerical result and test data with different water cement ratios and mineral admixture substitution ratios. Recently, Baert at al. (2011) presented the multicompound model for the hydration of Portland cement-fly ash binders. The reaction equations were deal with the theory of Powers which considered the hydration reactions of Portland cement and pozzolanic reaction of fly ash separately. The evaluation of the kinetic reaction of each clinker minerals was studied by the generally-known model, Avrami and Jander eqautions, to measure the isothermal heat producing by cement, fly ash, and water. The model explained the rate control of nucleation, phase boundary, and diffusion reactions. The kinetics of pozzolanic reactions was described by the similar equations and incorporated the parameters obtained from the test data. It was found from the study that fly ash may increase the reaction rate of clinker minerals and, at the same time, it can retard another mineral. Narmluk and Nawa (2011) studied the influence of fly ash on kinetic hydration reaction of Portland cement with different curing temperatures. The modified shrinking-core model was incorporated to determine the kinetic coefficients of the various hydration processes. The study showed that the hydration kinetics of cement were affected by fly ash replacement ratios and curing temperatures. At 20 ^{o}C and 35 ^{o}C, fly ash decreased the hydration rate of cement in the early period whereas it accelerated the hydration activity of cement in the later period. However, it was found at 50 ^{o}C that high replacement ratios of fly ash retarded the hydration of cement at the later ages. This is because, at higher temperature, the pozzolanic reaction of large volume of fly ash is strongly accelerated from early period. More recently, Zeng et al. (2011) proposed a synthetic model for cement hydration extent in blended cement pastes taking into account the dilution effect, local water cement ratio, augmentation effect, and heterogeneous nucleation effect of fly ash particles. The hydration reaction and pozzolanic activity of cement paste with two water binder ratios, 0.3 and 0.5, mixed with four fly ash contents, 0%, 20%, 40%, and 60%, were investigated. The non-evaporable water and calcium hydroxide content were evaluated by thermal gravity analysis (TGA) and pozzolanic reaction of fly ash was measured by selective dissolution method. The numerical results from the model were compared with test data. It showed that local water cement ratio, heterogeneous nucleation effects, and fly ash hydration have equivalent contribution to the total non-evaporable water content in blended cement pastes while calcium hydroxide content was influenced by fly ash hydration activity. The comparison between numerical results and experimental data showed a good agreement.

3 Research Methodology

3.1 Multi-components ionic transport in saturated fly ash blended concrete

The governing equations to be used in this project will be a modified version of equation (3). Several important aspects will be considered and included in the governing equations.

- Ion-ion interaction

Ionic transport in electrolytic solution is subject to the restraints imposed by mass balance, current conservation, and electro-neutrality in conjunction with a flow law. For ideal dilute solutions, these equations are well defined (Newman, 1973). However, for non-ideal systems such as the pore solution in concrete, they have to be modified by considering ion-ion and ion-solvent interactions. The conventional model considering ion-ion interactions is the Debye-Huckel model, which considers only long-range interactions between ions given by Coulomb's law applied to point charges and it is valid only for non-ideal dilute solutions. The estimate of upper limiting concentration of the Debye-Huckel model is 0.01 mol/l for a binary electrolyte. This concentration, however, is much lower than that observed in many pore solutions in concrete. There have been several new models suggested for concentrated solutions (Braunstein 1971; Clegg and Pitzer 1992; Li and Page 1998). Using some most recent models and test data, the electro-diffusive flux for each species can be calculated as follows:

$$J_k = -D_k \nabla C_k - z_k D_k \left(\frac{F}{RT}\nabla\phi\right) C_k - D_k C_k \frac{\nabla\gamma_k}{\gamma_k} \qquad (k\text{=1, 2… } n) \qquad (7)$$

where J_k is the ionic flux, γ_k is the activity coefficient which is the function of concentrations of ionic species (only for ideal-dilute solutions $\gamma_k \equiv 1$) and $\nabla(.) = \partial(.)/\partial x$ is the partial derivative operator with respect to *x*. The ionic transport equations will be derived in the project based on the mass balance using equation (7) as the flux expression. The anticipated results will be a set of governing equations (a modified version of equation (3)).

- Ionic binding

It is evident that chloride ions can be bound to concrete pore surface during their transport both physically and chemically. Physically, they stay on the pore surfaces because of the friction and attraction forces from the solid phase; and chemically, they react with the aluminate phases to form chloroaluminates. In order to take into account the ionic binding, the conventional mass balance equation may be modified by incorporating the binding term as follows (Li and Page, 2000),

$$\frac{\partial C_k}{\partial t} + \frac{\partial S_k}{\partial t} = -\nabla J_k \qquad (k\text{=1, 2… } n) \qquad (8)$$

where S_k is the concentration of bound ions. Equation (8) can also be applied to the case where there are chemical reactions taking place between ionic species within the pore solution or at the solid surface of the pore structure. Another way, a simple way to deal with the ionic binding is to use the so-called binding capacity in the conventional mass balance equation (Xi et al. 1995a; Xi and Bazant 1999). Both methods will be studied in the project.

3.2 Mathematical morphology for characterizing fly ash blended cement paste microstructure and ionic transport

Once the governing equations for the transport processes are established, determination of the materials parameters in the equations becomes an important task. As discussed earlier, the material parameters are effective properties at the meso-scale, and the resistance to the mass transfer processes depends on the physical and chemical properties of the microstructure of concrete. In this task, we will focus on physical aspect of the material models, which depends primarily on spatial characteristics of the microstructure (i.e. spatial distribution of the constituent phases). The transport and chemical characteristics of the material models (e.g. chloride diffusivity and ionic binding) will be developed for concrete containing fly ash.

First, the microstructure can be considered as a stochastic field. Then, how to describe mathematically the microstructure features and how to relate the mathematical features to the transport properties of the material are the two main research topics of this task. Morphological models will be developed to describe the statistical information of the microstructure. Then, transport models will be developed based on the obtained statistical information of the constituent phases of the concrete.

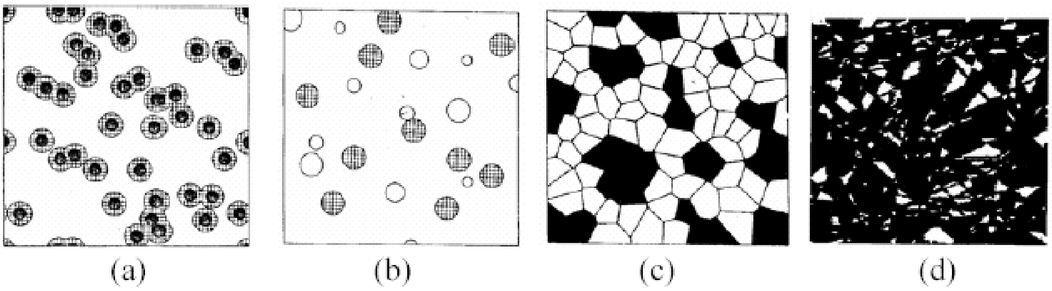


Fig. 2 Computer generated microstructures for cement paste and concrete, (a) Penetrable spherical model; (b) Non-penetrable spherical model; (c) S-mosaic for pore structure of cement paste; (d) L-mosaic for microstructure of cement paste.

- Morphological models

Spatial pattern of multiphase and multidimensional internal structures of most composite materials are highly random, quantitative description of the spatial distributions should be developed based on proper statistical models, which characterize the morphological features. Two different types of models have been developed for this purpose (Adler, 1981; Serra, 1982; Adler, 1992). One uses spherical units of either monosize or different sizes. The units can be non-penetrable or penetrable, i.e. with solid core and soft shell (Torquato, 1991). The simulated penetrable and non-penetrable models are shown in Fig. 2(a) and Fig. 2(b). This kind of models is actually a special case of the Boolean model in stereology (Serra, 1982, 1988), which is more general in that it includes basic units of different shapes, not just spheres, and can be used to simulate a wide variety of spatial structures. Another kind of models is called mosaic pattern in which a space or a plane is divided into polygons of 3D or 2D. Different dividing methods result in various spatial structures (Pielou, 1977).

Mosaic patterns will be used in this project. It is one of the morphological models that can be used for characterization of internal structures of concrete. Fig. 2(c) shows a S-mosaic which can be used for grain structure of low angularity. Fig. 2(d) shows a L-mosaic which can be used to simulate grain structure of high angularity. Mosaic patterns are also referred to as random tessellation. S-mosaic is also called Voronoi tessellation in mathematical morphology.

- High order correlation functions for transport processes

For a composite material with well dispersed constituent phases, the volume fractions of the phases have dominant effect on its transport properties, and other morphological parameters have only minor influences. However, when a transport process depends not on global information of the microstructure but primarily on local features, high order parameters must be taken into account, in addition to volume fractions of the phases, which is a kind of first order statistics. For instance, in the case of ionic penetration into concrete, the transport process takes place along the direction with the least resistance. Such a direction depends on the properties of the constituent phases at vicinity of the diffusion front rather than the whole body of the material, which means the local characteristics of the spatial arrangement of pores is more important than the information based on the global (long range) average. As a result, the morphological details of the microstructure must be taken into account.

The ions at a point in concrete, say Point A, may move along possible paths AB, AC, or AD. The actual mass transfer takes place always along the direction of the least resistance, therefore, to understand behaviour of the ionic transfer, the resistance along any of these two points must be known. The function characterizing behaviours of any two points in a stochastic field is called two-point correlation function, which depends on diffusion properties of the phases, as well as the statistical information of the spatial arrangement of the phases. For a more realistic description, the same diffusion front (i.e. at Point A) may be considered to move along possible paths ABB', ACC', or ADD' (B', C', and D' are the points further away from Point A). In this case, there are three points involved along each possible diffusion path. The corresponding correlation function is called three-point correlation function. It is clear that the resistance of the concrete to the ionic transfer is definitely related to the correlation function of its microstructure.

As described above, real diffusion paths in concrete are composed of multiple points, which means higher order correlation functions (above the second order function) must be established for a complete description of the transport process. The statistical parameters of the high order correlation functions will then be related to concrete mix design parameters, such as water-cement ratio and aggregate content and gradations. In this way, from concrete containing fly ash mix design parameters we can estimate the morphological feature of the microstructure. The high order correlation functions may be developed by two types of methods. One is to follow the procedure used by Torquato (1986) for spatial structures made of spherical units. The other is to apply the general role of Boolean model (Serra, 1982, 1988). Of course, both methods need to be further developed to take into account the details involved in mosaic patterns.

- Transport models based on higher order statistical parameters

Much has been done in composite mechanics on how to evaluate an effective transport property of a composite material based on volume fractions and transport properties of the constituents of the material. There have also been some studies on how to include higher order microstructure information in constitutive models for transport properties of composite materials in general (Torquato, 1992; Adler, 1992), but nothing has been done specifically for concrete. The existing methods will be modified for incorporating the morphological features in the material models for the ionic transport in concrete. A new method will also be developed based on random walk model, this is feasible because the mosaic patterns can be related to Markov chain model.

3.3 Determination of coupling parameters for multi-species transport in non-saturated concrete

- Non-saturated porous media

Most existing ionic transport models have been developed for saturated concrete structures in which ions move within the pore solution but the solution itself does not move. For most of concrete structures under service condition, this is not true because most of the structural members are in non-saturated state. Chloride penetration in non-saturated concrete will be different from that in saturated concrete (Ababneh et al. 2003). In this project, we will consider not only the effect of moisture movement in fly ash blended concrete, but also the coupling effect between moisture diffusion and chloride transfer. To this end, the flux of moisture in fly ash blended concrete, J_w, is assumed to consist of the flux due to the gradient of moisture concentration as well as the flux due to the gradient of chloride (see equation (9)); and the flux of chloride ions, J_{Cl}, is composed of a flux due to chloride concentration gradient and the flux due to moisture concentration gradient (see equation (10))

$$J_w = -D_w \nabla(w) - D_{w-Cl} \nabla(C_{Cl}) \tag{9}$$

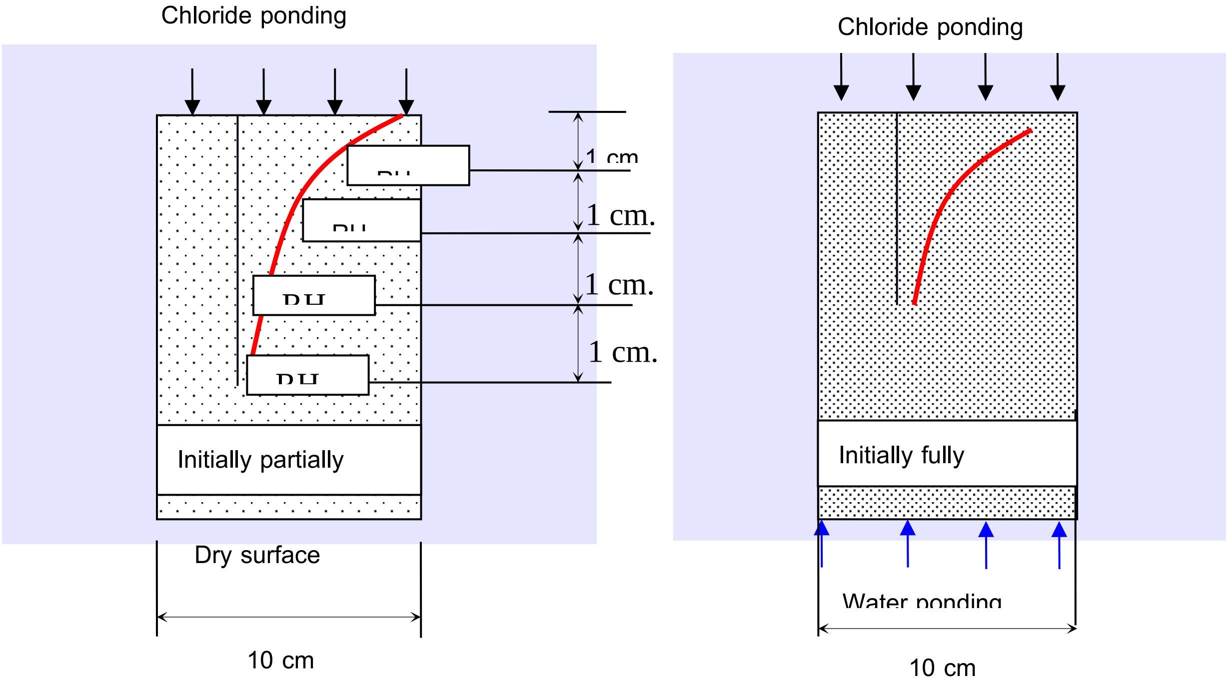
$$J_{Cl} = -D_{Cl-w} \nabla(w) - D_{Cl} \nabla(C_{Cl}) \tag{10}$$

in which w = water (or moisture) content in concrete; D_w = moisture diffusion coefficient; D_{Cl} = chloride diffusion coefficient; $D_{w\text{-}Cl}$ is the coupling parameter for the effect of chloride penetration on moisture diffusion, and $D_{Cl\text{-}w}$ the coupling parameter for the effect of moisture diffusion on chloride penetration. Both coupling parameters will be experimentally studied in the project. In the actual implementation, the second term on the right hand side of equation (10) needs to be replaced by equation (7) in order to take into account the ion-ion interaction. The modified forms of equations (7), (9), and (10) together with the mass balance equations will provide a complete set of governing equations for charactering the penetration of multi-components in non-saturated fly ash blended concrete structures.

In this project, the experiments will be conducted to determine the coupling parameters due to the coupled effect among chloride, other chemical species in concrete pore solution (Na^+, K^+, and OH^-), and moisture. The basic idea of the experimental study is shown in Fig. 3, which is a ponding test with two different experimental setups. The first setup is shown in Fig. 3(a), in which the concrete specimen is partially saturated and exposed to a NaCl solution on the top surface. Since the concrete is not fully saturated (the internal humidity in concrete is lower than 100%), there are two driving forces in the specimen for the moisture and chloride diffusion: moisture and chloride concentration gradients. The second setup is shown in Fig. 3(b), in which the concrete specimen is fully saturated and exposed to the same NaCl solution on the top surface and to water on the bottom surface. Since the concrete is fully saturated all the time, there is only one driving force in the specimen for the chloride diffusion (neglecting gravity force): the chloride concentration gradient. After a certain ponding period, the chloride concentration profiles in the two concrete specimens will be measured and compared. If the profile in specimen (a) is higher than that in specimen (b), the difference must be due to the moisture gradient in specimen (a). The same ponding test can be used for concrete specimens exposed to chloride solutions of different concentrations (3% and 5% are used in this study). Each concentration group contains five different amount of fly ash cement replacement, 0%, 15%, 25%, 35%, and 50%. The concentration profiles will be compared. If there is any difference in the profiles, it means that the coupling effect is concentration dependent.

The concrete samples are designed as ten-centimeter-diameter cylinders with heights of twenty centimeters, respectively. The samples used for the non-saturated concrete are embedded with SHT75 Sensirion humidity and temperature sensors. These sensors are used to measure humidity profiles in the concrete, which provide necessary information for determining the coupling parameter $D_{Cl\text{-}H}$. The sensors are wrapped in GorTex fabric before the concrete is poured around them. The fabric is used to protect the sensors as well as allow a breathable interface so that the humidity readings will be accurate. Four sensors are placed in each sample as shown in Fig. 3(a), the first sensor was placed at the one centimeter from the top solution surface; the second sensor was placed two centimeters from the top solution surface; the third sensor was placed three centimeters from the top solution surface; and the fourth sensor was placed four centimeters from the top solution surface. The samples are cast, de-molded after 24 hours and store in the moist room for 28 days.

The concrete samples exposed to the NaCl solutions are removed from the solutions after three exposure periods: 7 days, 15 days, 30 days, 60 days and 90 days, and allow to dry for one day at room temperature. Samples of concrete will be used to evaluate chloride concentration by existing method.



(a) Initially partially saturated specimen
the top surface is exposed to NaCl solution

(b) Initially fully saturated; specimen;
the top surface is exposed to NaCl solution

Fig. 3 The basic idea of the experimental study for determining the coupling parameters

So far, there has been no material models developed for the coupling parameters between ion transport and moisture diffusion in fly ash blended concrete, $D_{H\text{-}i}$ and $D_{i\text{-}H}$. The experimental results from described above will be used here to develop models for the coupling parameters. There are no experimental data or material models of coupling parameters for other species, Na^+, Ca^{2+}, OH^-, and K^+ transport in non-saturated concrete containing fly ash. As the first approximation, the coupling parameters of these ionic species can be evaluated based on the results for chloride ions. For example, the effect of moisture on ionic diffusions can be considered as the same constant, ε, 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, the coupling parameter can be expressed as:

$$D_{i-H} = \varepsilon C_f = \varepsilon C_i \qquad (11)$$

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, δ, 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, $D_{H-Cl_f} \big/ D_{Cl} = D_{H-C_i} \big/ D_i$. 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, δ_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):

$$\frac{D_i}{D_{Cl}} = \frac{D_{H-C_i}}{D_{H-Cl_f}} = \frac{\delta_i C_i}{\delta C_f} \qquad (12)$$

3.4 Determination of coupling parameters for multi-species transport in non-isothermal concrete

Most reinforced concrete structures such as bridge decks, marine structures, and concrete structures subjected to harmful chloride ions are also subjected to variation of temperature. The durability of these structures is affected by the coupled diffusion of chloride and temperature. If the temperature is constant on both sides of the structures, the temperature diffusion is neglected. However, the most common scenario is when the structures are subjected to heating from one side. This can lead to heat transfer from the highest to the lowest temperature. The heat transport accelerates the diffusion rate of chloride ions. A review of available literatures shows that most the experiments for chloride penetration are conducted at room temperatures. However, in 1879 the Swiss scientist Charles Soret found that the salt concentration did not remain consistent when salt solution was placed in a tube with the two ends at different temperatures. This effect is called the “Soret effect”. The salt concentration was higher near the cold end than near the hot end of the tube. The conclusion is that the temperature gradient caused the flux in the salt concentration.

Mathematically, based on the Nernst-Planck equation, the flux of each ion in fly ash blended concrete, J_i, is assumed to consist of the flux due to the gradient of ionic concentration as well as the flux due to the gradient of temperature (see equation (11)); and, based on the Fourier’s law of heat conduction, the heat flux, J_Q, is composed of a flux due to temperature gradient and the flux due to ionic concentration gradient (see equation (12))

$$J_i = -D_i \nabla C_i - z_i D_i \left(\frac{F}{RT} \nabla \phi \right) C_i - D_{i-T} \nabla T \qquad (11)$$

$$J_Q = -D_{T-T} \nabla T - D_{T-i} \nabla C_i \qquad (12)$$

where J_i is the flux of species i, D_i is the diffusion coefficient of species i, C_i is the concentration of species i in the solution, z_i is the charge number of species i, F is the Faraday constant, R is the gas constant, T is the temperature of material, and Φ is the electrostatic potential. J_Q is the heat flux, $D_{T\text{-}T}$ is the thermal diffusivity of concrete, and T is temperature. $D_{i\text{-}T}$ is the coupling parameter due to influence of temperature on ion diffusion and $D_{T\text{-}i}$ is the coupling parameter of the effect of ionic diffusion on temperature. Although there are two coupling effect parameters only one is studied that is the effect of heat transfer on ion penetration. Based on the literature reviews, the ionic concentration gradient has very small influence on heat transport. Therefore, the coupled effect due to the influence of ionic diffusion on temperature variation, so-called latent heat diffusion, can be neglected. To this end, the coupling parameter "$D_{T\text{-}i}$" is not considered in this project. The experimental study will be conducted to determine the coupling parameter due to the effect of heat transport on ion diffusion, $D_{i\text{-}T}$. In order to better understand the effect of temperature gradient on chloride concentration, the experimental study will include the influence of fly ash as cement replacement, water cement ratio and concentration dependence on the chloride penetration. So, three series of experiments will be conducted. The first series will incorporate the concentration of 3% NaCl, with three temperature gradients. The second series will be repeated the first series using a 5% chloride concentration with the same temperature gradients. The third series will be included the same temperature gradients as the first series but with a lower water cement ratio for the concrete containing fly ash. Each series consists of five different amount of fly ash cement replacement, 0%, 15%, 25%, 35%, and 50%. The summarization of the experimental study program is shown in Fig. 4.

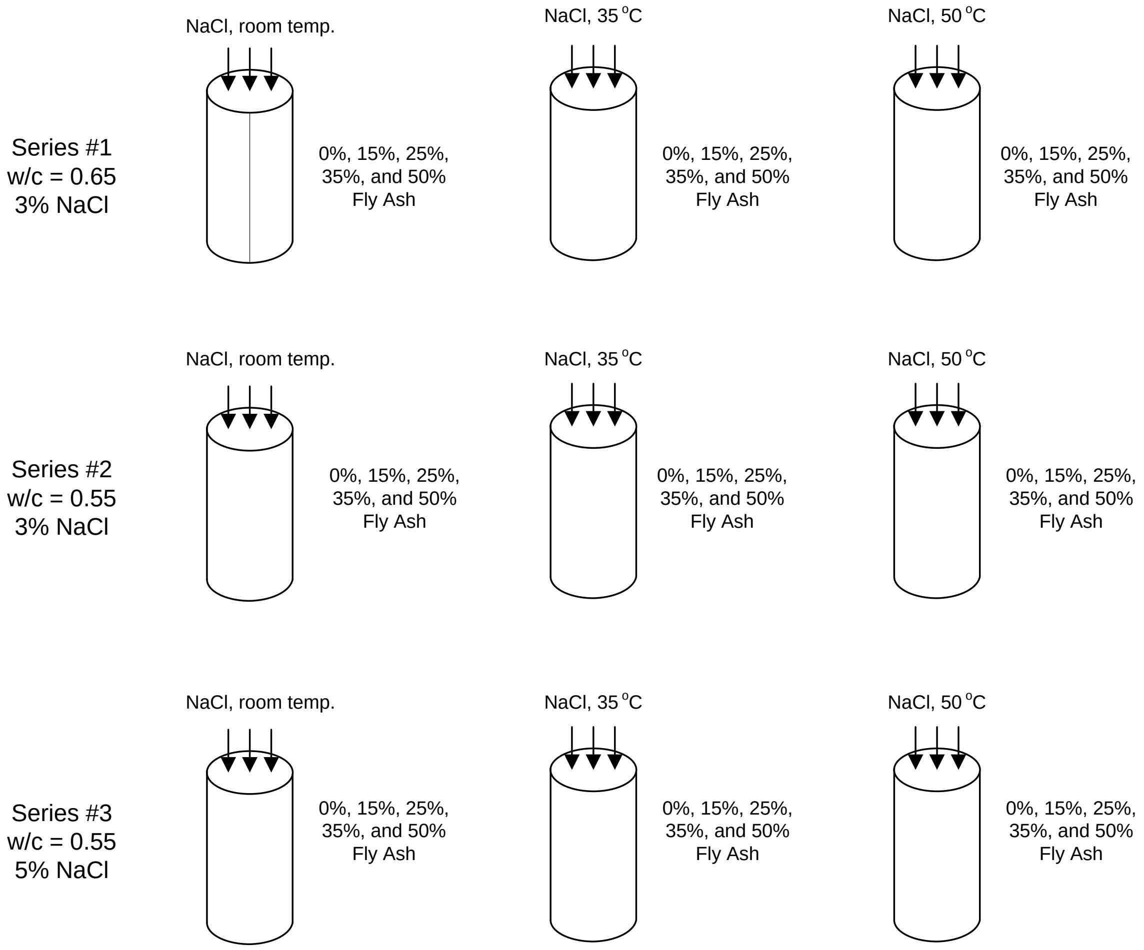


Fig. 4 The summarization of the experimental study program

3.5 Influence of temperature on multi-ionic species diffusion in saturated concrete

Many mathematical models have been developed to predict chloride ions transport in concrete structures. Under saturated condition, chloride penetration into concrete is mainly driven by concentration gradients of various diffusing ions in concrete. Under non-saturated condition, chloride penetration into concrete is driven not only by the concentration gradients but also by moisture gradient, and many studies have shown that the moisture transport has a significant effect on the chloride diffusion in concrete (Ababneh et al., 2003; Abarr, 2005; Suwito et al., 2006). Similarly, the moisture diffusion is influenced by the chloride penetration which accelerates the rate of moisture diffusion (Ababneh and Xi, 2002). Under actual service condition, reinforced concrete structures are exposed to an environment with deicing salts, moisture variation, and temperature fluctuation. In this case, not only the moisture diffusion has an influence on the chloride transport, the temperature variation also has an effect on the chloride penetration.

The temperature effect has not been investigated by many researchers. Recently, Isteita (2009) conducted an experimental study on the temperature effect on chloride transport in concrete.

It was found that the thermal effect contributed significantly to chloride penetration mechanism. With an increasing temperature, the rate of chloride penetration increased. A coupling parameter for the effect of temperature on the chloride transport was developed in the study. Over the years, there have been mathematical and numerical models developed to investigate chloride ions transport as well as multi-ionic transport in concrete, but there has been little research on the temperature effect. Yu and Page (1996), and Li and Page (1998, 2000) developed a mathematical model to simulate electrochemical chloride removal (ECR) from concrete and then Wang et al. (2005) applied the ECR model to perform the simulation of the mechanism of chloride ingress into concrete. Samson et al. (1999a) conducted a theoretical study on ion diffusion mechanisms in cement-based materials. Later on, Samson and Marchand (1999b) presented the mathematical model of ion diffusion mechanisms in porous media based on the Extended Nernst-Planck equation which accounts for electrostatic potential gradient. Recently, Marchand (2001) and Samson and Marchand (2007) developed a simulation model of multi-ionic transport in unsaturated cement-based materials exposed to aggressive chemical environments called STADIUM®. The mechanism of chloride penetration into non-saturated concrete was also investigated by Nguyen et at. (2006). The governing equations of the model were derived based on the Nernst-Planck and electroneutrality equations. Then, the numerical results obtained from the model were compared with test data and a good agreement was observed.

As the actual condition of concrete structures exposed to various chloride environments is most likely non-isothermal rather than isothermal, the temperature variation has significant effect on the transport properties and chemical reaction of ions. In this study, we developed a mathematical model to predict the influence of temperature on chloride penetration into saturated concrete structures. The moisture diffusion was not considered in the model, while the effect of other ions in concrete pore solution was taken into account such as, Na^+, K^+, and OH^-. And, the governing equation of temperature was described in terms of Fouries's law. Differing from those models proposed by saetta et al. (1993) and Martin-Perez et al. (2000) in which temperature dependent transport parameters were used for the thermal effect, the present model took into account the coupled effect of temperature on chloride transport by an explicit term in the ionic flux equations. There was a coupling parameter associated with the explicit term which was incorporated in the governing equations, and the value of coupling parameter and the model for the coupling parameter were obtained from Isteita study (2009). The governing equations were solved by the finite element method. The numerical results obtained from the present model were compared with available test data. The model can be applied to predict chloride penetration into saturated concrete structures under non-isothermal condition.

- **Basic Formulation**

The formulation of mathematical models for chloride transport can be done by two different approaches. One is based on Fick's first and second laws which is related to the diffusion mechanism at macroscopic level (Ababneh, 2003; Saetta et al.; 1993a, 1993b; Frey et al., 1994; Sergi et al., 1992; Berke et al., 1994; Tang and Nilsson, 1993; Wee et al., 1997; Xi and Bazant, 1999; Suwito and Xi, 2004). This type of formulation is convenient for considering the single ion (the chloride ion) transport in concrete. The other formulation is based on the Nernst-Planck equation which takes into account the electro-chemical coupling phenomena. This type of formulation is necessary for characterizing the fully coupled multi-ionic transport in concrete. In the present study, the formulation of chloride ions and other chemical species in concrete pore solution, Na^+, K^+, and OH^-, is based on the Nernst-Planck equation. The governing equation of heat flow is described by the Fourier's law of heat conduction.

The flux of each ionic species in a porous media without thermal effect can be expressed as:

$$J_i = -D_i \nabla C_i - z_i D_i \left(\frac{F}{RT} \nabla \phi \right) C_i \tag{13}$$

where J_i is the flux of species i, D_i is the diffusion coefficient of species i, C_i is the concentration of species i in the solution, z_i is the charge number of species i, F is the Faraday constant, R is the gas constant, T is the temperature of material, and Φ is the electrostatic potential. The mass balance equation for each ionic species can be written as:

$$\frac{\partial C_t}{\partial t} = \frac{\partial (C_i + S_i)}{\partial t} = -\nabla J_i \tag{14}$$

By substituting Eq. (1) into Eq. (2), it gives:

$$\frac{\partial C_t}{\partial t} = \frac{\partial (C_i + S_i)}{\partial t} = \frac{\partial C_t}{\partial C_i}\frac{\partial C_i}{\partial t} = \nabla \left(D_i \nabla C_i + z_i D_i \left(\frac{F}{RT} \nabla \phi \right) C_i \right) \tag{15}$$

in which C_t is the total chloride ion concentration which is the summation of free chloride ion (C_i) and bound chloride ion (S_i). When chloride ions penetrate into concrete, some of them can have chemical reaction with cement components and some of them can attach to the pore wall, and these chloride ions are called bound chloride. The others are free to move through interconnected pores in concrete which are called free chloride. $\partial C_t/\partial C_i$ is the chloride binding capacity. The binding capacity is applied only to chloride ion not to other species, Na^+, K^+, and OH^- (will be discussed in the section of material models), and thus there is no subscript i for C_t. The binding capacity is related to the ratio of the free and bound chloride, and this parameter will be explained in the next section.

In order to solve the Nernst-Planck equation, another relation accounted for the electrostatic potential induced by ionic interaction is required. The electrostatic potential can be determined based on three different methods. Samson and Marchand (2001) solved the electrostatic potential for ion transport in cement-based materials by using Poisson's equation. As mentioned by Samson et al. (1999a), the Poisson's equation can be used in more general cases. The nil current assumption was used by Li and Page (2000) and Wang et al. (2005). This method is based on the fact that there is no net current flow within the concrete pore solution due to the coupled ionic transport. The third method is based on electroneutrality condition (i.e. the total charge of all ions in concrete is zero), which will be used in the present study. The electroneutrality equation can be expressed as:

$$\sum_{i=1}^{n} C_i z_i = 0 \tag{16}$$

in which C_i is the concentration of species i, z_i is the charge number of species i, and n is the number of ionic species. The main advantages of using electroneutrality condition are the simplified governing equations, reduce computational time, and less difficulty in computational schemes than the other two methods (Wang et al., 2005; Nguyen et al., 2006). The comparison among the nil current, Poisson's equation, and electroneutrality condition used in modeling of chloride penetration into concrete was investigated by Nguyen et al. (2006) and Damrongwiriyanupap et al. (2011).

For the heat flow in concrete material, the heat flux can be simply expressed by Fourier's law of heat conduction equation:

$$J_Q = -D_{T-T} \nabla T \tag{17}$$

in which J_Q is the heat flux, D_{T-T} is the thermal diffusivity of concrete, and T is temperature. The mass balance equation of heat flow is written as:

$$\frac{\partial Q}{\partial t} = -\nabla J_Q \tag{18}$$

Combining Eqs. (5) and (6), the partial differential equation (PDE) governs the heat flow in concrete can be defined as:

$$\frac{\partial Q}{\partial t} = \frac{\partial Q}{\partial T}\frac{\partial T}{\partial t} = \nabla\left(D_{T-T} \nabla T\right) \tag{19}$$

where $\partial Q / \partial T$ is the heat capacity of concrete. In order to take into account the temperature effect on the transport of ions in concrete, the mass balance equations of each ionic species need to be reformulated. There are two ways to perform it. One is to use temperature dependent transport parameters in Eq. (15), and the other is to add an explicit term in Eq. (15) for the thermal effect. The latter method is used in the present study. The advantage is that the material models developed for the transport parameters in Eq. (15) under isothermal condition can be used, and the thermal effect is considered by the additional term. To this end, the original Nernst-Planck equation, Eq. (15), is modified as

$$\frac{\partial C_t}{\partial t} = \frac{\partial (C_i + S_i)}{\partial t} = \frac{\partial C_t}{\partial C_i}\frac{\partial C_i}{\partial t} = \nabla\left(D_i \nabla C_i + z_i D_i \left(\frac{F}{RT}\nabla \phi\right) C_i + D_{i-T} \nabla T \right) \tag{20}$$

in which $D_{i\text{-}T}$ is the coupling parameter due to influence of temperature on the diffusions of ions. A model for this parameter will be described in the next section based on the experimental study of temperature effect on chloride penetration into saturated concrete by Isteita (2009). The effect of ionic diffusion on the heat conduction is considered as insignificant and thus not included in Eq. (19).

- **Material Models**

In order to solve the governing equations, Eqs. (19) and (20), and the electroneutrality condition, Eq. (16), the material parameters involved in the equations must be determined first. These material parameters are ionic diffusion coefficients, ionic binding capacities, and the coupling parameters. In general, the material parameters depend on mix design and age of concrete and they are not constants. For instance, the chloride diffusion coefficient depends on water-cement ratio, curing time, aggregate content and microstructure of cement paste, which in turn depends on concrete mix design parameters and age of concrete. In the present study the chloride diffusion coefficient is characterized by a material model proposed by Xi and Bazant (1999) which takes into account these influential parameters. Similarly, the chloride binding capacity can be described by the material model developed by Xi and Bazant (1999). A material model for the coupling parameter for the temperature effect will be developed based on available experimental results. For reader's convenience, the previously developed transport parameters will be introduced briefly, and then the model for the coupling parameter will be described in detail.

  - **Chloride Diffusion Coefficient (*D_{Cl}*)**

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

$$D_{Cl} = f_1(w/c,t_0)\, f_2(g_i)\, f_3(T)\, f_4(C_f) \tag{21}$$

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):

$$f_1 = \frac{28-t_0}{62{,}500} + \left(\frac{1}{4} + \frac{(28-t_0)}{300}\right)\left(\frac{w}{c}\right)^{6.55} \tag{22}$$

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 phase composite model developed by Christensen (1979):

$$f_2(g_i) = D_{cp}\left(1 + \frac{g_i}{(1-g_i)/3 + 1/\left(\left(D_{agg}/D_{cp}\right)-1\right)}\right) \tag{23}$$

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):

$$D = \frac{2\left(1-\left(V_p - V_p^c\right)\right)}{S^2}\left(V_p - V_p^c\right)^{4.2} \tag{24}$$

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. (12) 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 (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, 1994b). The diffusivity of aggregates, D_{agg}, can be taken as a constant, and a proposed value is $1\text{x}10^{-12}$ cm^2/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:

$$f_3(T) = \exp\left[\frac{U}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \tag{25}$$

in which U is the activation energy of the diffusion process, R is the gas constant (8.314 J mol^{-1} K^{-1}), T and T_0 are the current and reference temperatures, respectively, in Kelvin (T_0 = 296 K). According to the studies by Page et al. (1981) and Collepurdi 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.

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	-

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:

$$f_4(C_f) = 1 - k_{ion}(C_f)^m \tag{26}$$

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. (26) and all following equations that C_f is used to represent the free chloride concentration and C_i is for ionic concentration of all other ions.

- **Chloride Binding Capacity** $\left(\partial C_f / \partial C_t\right)$

As mentioned before, the ionic binding capacity is considered only for chloride ions. Other chemical species in concrete pore solution are assumed to be no binding capacity. The total chloride concentration, C_t, is the summation of free chloride, C_f, and bound chloride, C_b, which can be given by:

$$C_t = C_f + C_b \tag{27}$$

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

$$\frac{dC_f}{dC_t} = \frac{1}{1+\frac{dC_b}{dC_f}} \tag{28}$$

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:

$$\frac{dC_f}{dC_t} = \frac{1}{1+\frac{A10^B \beta_{C-S-H}}{35{,}450\beta_{sol}}\left(\frac{C_f}{35.45\beta_{sol}}\right)^{A-1}} \tag{29}$$

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, β_{sol} and β_{C-S-H}.

The parameter β_{sol} is described as the relationship between the volume of pore solution and weight of concrete (*L/g*):

$$\beta_{sol} = \frac{V_{sol}}{w_{conc}} = \frac{w_{sol}}{\rho_{sol} w_{conc}} = \frac{n(H,T)}{\rho_{sol}} \tag{30}$$

where V_{sol} is the volume of pore solution, w_{sol} is the weight of pore solution, w_{conc} is the weight of concrete, ρ_{sol} is the density of the pore solution (*g/L*) and is dependent on chloride concentration. To simplify the calculation, the parameter ρ_{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:

$$n(H,T) = f_{cp} n_{cp}(H,T) + f_{agg} n_{agg}(H,T) \tag{31}$$

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 β_{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:

$$\beta_{C-S-H} = \frac{w_{C-S-H}}{w_{total}} \tag{32}$$

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 β_{C-S-H} can be found in the paper by Xi (1994a).

The limitation of binding capacity based on the Freundlich isotherm, Eq. (29), 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 starts. 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. (29) based on Freundlich isotherm. The Langmuir isotherm is expressed as:

$$\frac{1}{C_b^{'}} = \frac{1}{k^{'} C_{bm}} \frac{1}{C_f^{'}} + \frac{1}{C_{bm}} \tag{33}$$

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. (33). 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:

$$C_b^{'} = \frac{1{,}000 C_b}{\beta_{C-S-H}} \tag{34}$$

$$C_f^{'} = \frac{C_f}{35.45 \beta_{sol}} \tag{35}$$

Substituting Eqs. (34) and (35) into Eq. (33), yields

$$\frac{1}{C_b} = \frac{1{,}000}{\beta_{C-S-H}} \left[\frac{35.45 \beta_{sol}}{k^{'} C_{bm}} \frac{1}{C_f} + \frac{1}{C_{bm}} \right] \tag{36}$$

Eq. (36) can be re-expressed in a simple form as

$$C_b = \frac{1}{\beta + \frac{1}{\alpha C_f}} \tag{37}$$

in which,

$$\alpha = \frac{k^{'} C_{bm} \beta_{C-S-H}}{35{,}450 \beta_{sol}} \tag{38}$$

$$\beta = \frac{1{,}000}{\beta_{C-S-H} C_{bm}} \tag{39}$$

Derivative of Eq. (37) with respect to C_f yields

$$\frac{dC_b}{dC_f} = \frac{1}{\alpha \left(C_f \right)^2 \left(\beta + \frac{1}{\alpha C_f} \right)^2} \tag{40}$$

By substituting Eq. (40) into Eq. (28), the binding capacity based on Langmuir isotherm can be expressed as:

$$\frac{dC_f}{dC_t}=\frac{1}{1+\frac{dC_b}{dC_f}}=\frac{1}{1+\frac{1}{\alpha\left(\beta C_f+\frac{1}{\alpha}\right)^2}} \quad (41)$$

Eq. (41) is used to calculate the binding capacity when free chloride concentration tends to zero, then the binding capacity is $1/(1+\alpha)$. The parameter α can be calculated by using Eq. (38) and is dependent on many factors. As a result, α 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 $C_{bm}=5.4083$.

- **Coupling Parameter (D_{i-T})**

The coupling parameter presented in this study was proposed by Isteita (2009). The parameter was evaluated based on the experimental study of temperature effect on chloride penetration into saturated concrete. The results from the experiment showed that the effect of temperature on chloride diffusion is very significant and the coupled effect of temperature on chloride diffusion in concrete should be taken into account. The influence of temperature on ions diffusion is related to Soret effect, which is the occurrence of a diffusion flux due to the temperature gradient. Then, the coupling parameter was derived by using a multifactor approach. It was also found that the coupling parameter was not constant but depended on chloride concentration, age of concrete, and temperature. This can be obtained by curve fitting of the test data written as:

$$D_{Cl-T}=5x10^{-8}C_f\, f_1(t)\, f_2(T) \quad (42)$$

Based on the Soret effect, the heat flow in concrete can carry not only chloride ions but also other ions in concrete pore solution so that we may apply this coupling parameter to all ionic species (Cl^-, Na^+, K^+, and OH^-), it gives,

$$D_{i-T}=D_{Cl-T}=5x10^{-8}C_f\, f_1(t)\, f_2(T) \quad (43)$$

in which D_{i-T} is the coupling parameter due to temperature effect on each ionic species i; C_f is the free chloride concentration; the first factor, $f_1(t)$, is the factor accounting for the age effect of concrete which is relevant to hydration reactions of cement paste given by Eq. (44):

$$f_1(t)=4t^{-1} \quad (44)$$

where t is the age of concrete. The second factor, $f_2(T)$, takes into account the influence of temperature which is described by the definition of Arrhenius's law:

$$f_2(T)=Exp(0.1\frac{U}{R}(\frac{1}{T_{ref}}-\frac{1}{T})) \quad (45)$$

where U is the activation energy of the diffusion process; R is the gas constant; and T and T_{ref} are current and reference temperature, respectively.

3.6 Multi-Ionic Species Diffusion in Non-saturated and Non-isothermal Concrete

One of the theoretical models for predicting chloride ingress into concrete structures is based on Fick's second law, leading to a simple solution of one-dimensional linear ordinary partial differential diffusion equation (Detwiler et al., 1999; Tamimi et al., 2008; Vu and Stewart, 2000). The main problem of the simplified linear models is that the apparent diffusion coefficient in the model, D_a, has to be considered as a constant. In fact, it is not a constant and it varies by more than one order of magnitude and depends on many factors such as material characteristics and surrounding exposure conditions of structures. As a result, we cannot use the constant diffusion coefficient of concrete to reliably predict the service life of structures which have been exposed to a corrosive environment. Also, the apparent diffusion coefficient of concrete for a given location cannot be applied to use for another circumstances (Marchand and Samson, 2009). Furthermore, if the variations of initial and boundary conditions such as moisture and temperature surroundings were to be taken into account the prediction error of using the Fick's second law could be even larger. It was emphasized by Marchand and Samson (2009) that Fick's model can only be appropriately used for concrete structures in saturated condition. However, the chloride exposure conditions of actual concrete structures are often found to be non-saturated and non-isothermal. To solve this problem, some Fick's models have been modified to account for moisture and temperature effects (Ababneh et al., 2003; Saetta, 1993; Suwito et al., 2006). This can be done either by using moisture and temperature dependent transport parameters or by incorporating the coupling terms in the chloride flux equation, which is adopted for the present study.

In saturated and isothermal conditions, chloride ions diffuse in concrete mainly due to its own concentration gradient. This means that there are no moisture and temperature effects on chloride penetration mechanism. On the contrary, the coupled diffusion process of chloride and moisture was evident in non-saturated condition that the rate of chloride diffusion was accelerated by moisture gradient. Similarly, moisture flow was affected by the chloride transport mechanism (Ababneh and Xi, 2002; Abarr, 2005). For non-isothermal condition, chloride transport mechanism in concrete is driven by not only its concentration gradient but also temperature variation gradient. It was emphasized by Isteita (2009) study that, by increasing temperature, the rate of chloride ingress into concrete can be increased.

Over the years, modeling of chloride transport in non-saturated concrete has been studied by many researchers. Saetta et al. (1993) proposed a numerical model of chloride penetration in partially saturated concrete. The model included the coupling effect of moisture movement on chloride diffusion. The transport equations of chloride and moisture were then solved using the finite element method. In 2000, Nilsson (2000) developed a chloride diffusion model for the concrete exposed to seawater splash or deicing salts. It was found from the study that diffusion and convection mechanisms of chloride could be explained as a function of moisture content in concrete. Ababneh et al. (2003) presented a mathematical model of chloride ingress into concrete in non-saturated condition. The coupling term for the moisture movement was incorporated in the diffusing equation of chloride. The two coupled partial differential equations of chloride and moisture were analyzed using the finite difference method. The numerical results are validated against the available test data and the verification showed that the model could be used to simulate and predict chloride diffusion in non-saturated concrete satisfactorily. Nielsen and Geiker (2003) proposed a simplified Fick's model to examine chloride penetration into partially saturated concrete and studied the relationship between chloride diffusion coefficient and degree of saturation. Their findings showed that the chloride diffusion coefficient depends on degree of saturation of concrete. Conciatori et al. (2010) presented a comprehensive model called "TransChlor" for simulating chloride diffusion associating with heat transfer, liquid and vapor movement, and carbon dioxide transport in concrete. Chloride profiles predicted by this model were validated with the experimental data and a good agreement was observed. Recently, Lin et al. (2010) established a systematic and numerical model for predicting service life of concrete structures subjected to chloride attack. The effect of moisture transport on chloride diffusion was included in the chloride flux equation which was represented as the degree of water saturation. The numerical results obtained from the model showed that the service life of structures exposed to drying and wetting circumstances is significantly different from that under the saturated condition. Based on these studies, it can be concluded that moisture variation has a remarkable influence on degradation of concrete structures causing by chloride attack.

As noticed from the above review, most of the mathematical models have been focused on chloride diffusion in non-saturated concrete, and the temperature effect on chloride transport has not been well investigated. The temperature variation is very significant and must be included in the mathematical model. A recent experimental study conducted by Isteita (2009) showed that the rate of chloride penetration is accelerated by temperature gradients. The temperature variation has a significant effect on not only the chloride transport but also on moisture movement. This can be described by Khoshbakht et al. (2009) study that moisture diffusion in masonry walls is significantly influenced by heat transfer. However, there is no available mathematical model taken into account the influences of temperature variation on simultaneous chloride and moisture diffusion in concrete. Therefore, in this study, a transport model based on Fick's law taking into account the fully coupled chloride, moisture, and heat flow in non-saturated and non-isothermal concrete is developed. The coupling parameters related to chloride, moisture, and heat transport in concrete are characterized and explicitly incorporated in the governing equations. The governing equations are then solved numerically by the finite element method. The validation is performed by comparing the numerical results obtained from the present model with the available test data and a good agreement is observed.

- **Basic Formulation of Governing Equations**

The flux of chloride ions through porous concrete depending on the concentration gradient is described by the Fick's law as follows:

$$J_{Cl} = -D_{Cl} \nabla C_f \qquad (46)$$

in which J_{Cl} is the flux of chloride ions, D_{Cl} is the diffusion coefficient of chloride ions, C_f is the free chloride concentration.

The total amount of moisture contained in concrete so-called moisture content is generally represented by water content (*w*) or by pore relative humidity (*H*). In the present study, the moisture content in concrete is presented by pore relative humidity which consists of amount of liquid water and water vapor existing in concrete pores (Bazant and Najjar, 1972). The moisture flux (J_H) can be described in terms of the gradient of pore relative humidity given by:

$$J_H = -D_H \nabla H \qquad (47)$$

where D_H is the humidity diffusion coefficient. Heat flow in concrete is described by the well-known Fourier's law of heat conduction giving the heat flux in function of gradient of temperature:

$$J_Q = -D_T \nabla T \qquad (48)$$

where J_Q is the heat flux, D_T is the thermal diffusivity of concrete, and T is temperature. As indicated earlier, in order to describe the coupled transport processes involving chloride, moisture, and temperature, the above listed three governing equations can be modified by adding new terms expressed explicitly in terms of the gradients of the state variables, and as a results, the three governing equations will become fully coupled and then these coupled equations must be solved simultaneously. For example, the flux of chloride ions (J_{Cl}), Eq. (46), in non-saturated and non-isothermal concrete can be written as:

$$J_{Cl} = -\left(D_{Cl} \nabla C_f + D_{Cl-H} \nabla H + D_{Cl-T} \nabla T\right) \qquad (49)$$

in which $D_{Cl\text{-}H}$ and $D_{Cl\text{-}T}$ are the coupling parameters corresponding to the effect of moisture and temperature variation on the chloride diffusion, respectively. Similar to chloride flux, the coupling terms are also included in moisture and heat flux. Then, Eqs. (47) and (48) can be rewritten as:

$$J_H = -\left(D_{H-Cl} \nabla C_f + D_H \nabla H + D_{H-T} \nabla T\right) \qquad (50)$$

$$J_Q = -\left(D_{T-Cl} \nabla C_f + D_{T-H} \nabla H + D_T \nabla T\right) \qquad (51)$$

where $D_{H\text{-}Cl}$, $D_{T\text{-}Cl}$, $D_{H\text{-}T}$, and $D_{T\text{-}H}$ are coupling parameters. In general, coupling parameter $D_{i\text{-}j}$ represents the effect of *j* process on the *i* process.

The mass balance equations of chloride, moisture, and heat transport in concrete are given by Eqs. (52), (53), and (54), respectively:

$$\frac{\partial C_t}{\partial t} = \frac{\partial C_t}{\partial C_f}\frac{\partial C_f}{\partial t} = -\nabla J_{Cl} = \nabla\left(D_{Cl} \nabla C_f + D_{Cl-H} \nabla H + D_{Cl-T} \nabla T\right) \qquad (52)$$

$$\frac{\partial w}{\partial t}=\frac{\partial w}{\partial H}\frac{\partial H}{\partial t}=-\nabla J_H=\nabla\left(D_{H-Cl}\nabla C_f+D_H\nabla H+D_{H-T}\nabla T\right) \tag{53}$$

$$\frac{\partial Q}{\partial t}=\frac{\partial Q}{\partial T}\frac{\partial T}{\partial t}=-\nabla J_Q=\nabla\left(D_{T-Cl}\nabla C_f+D_{T-H}\nabla H+D_T\nabla T\right) \tag{54}$$

in which $\partial C_t/\partial C_f$, $\partial w/\partial H$, and $\partial Q/\partial t$ represent the chloride binding capacity, moisture capacity, and heat capacity, respectively. The coupling parameters corresponding to the coupled transport mechanisms among chloride, moisture, and temperature will be explained later.

- **Material Models**
  - **Moisture diffusion coefficient**

The moisture diffusion coefficient of concrete can be characterized using the theoretical formulation of composite-based materials derived by Christensen (1979) expressed as:

$$D_H=D_{H_{cp}}\left(1+\frac{g_i}{\frac{(1-g_i)}{3}+\frac{1}{\left[(D_{H_{agg}}/D_{H_{cp}})-1\right]}}\right) \tag{55}$$

in which g_i is the volume fraction of aggregates, D_{Hcp} is the moisture diffusivity of the cement paste and D_{Hagg} is the moisture diffusivity of the aggregates. It is due to the fact that the rate of moisture diffusion through discontinuous pores appeared in aggregates is much slower that in cement paste. Therefore, D_{Hagg} in Eq. (55) can be neglected. The moisture diffusivity of cement paste can be evaluated by the empirical model proposed by Xi et al. (1994).

  - **Moisture capacity**

The moisture capacity of concrete can be simply calculated by taking the proportion of the moisture capacities of cement paste and aggregate as proposed by Xi et al. (2000):

$$\frac{dw}{dH}=f_{agg}\left(\frac{dw}{dH}\right)_{agg}+f_{cp}\left(\frac{dw}{dH}\right)_{cp} \tag{56}$$

where f_{agg} and f_{cp} are the weight percentages of the aggregate and cement paste, respectively; $(dw/dH)_{agg}$ and $(dw/dH)_{cp}$ are the moisture capacity of aggregate and cement paste, respectively. The parameters given in Eq. (56) can be determined based on the model developed by Xi et al. (1994) and Xi (1995).

- **Coupling parameters**

In this study, the fully coupled transport equations of chloride, moisture, and heat are formulated based on modified Fick's law. The coupling terms are explicitly incorporated in the governing equations as illustrated in Eqs. (52), (53), and (54).There are mainly six coupling parameters: 1) the effect of moisture on chloride transport (D_{Cl-H}), 2) the effect of chloride on moisture transport (D_{H-Cl}), 3) the influence of heat conduction on chloride transport (D_{Cl-T}), 4) the influence of heat conduction on moisture transport (D_{H-T}), 5) the effect of chloride transport on heat conduction

($D_{T\text{-}Cl}$), and 6) the influence of moisture transport on heat conduction ($D_{T\text{-}H}$). The detail of these parameters will be explained as follows.

- **$D_{Cl\text{-}H}$ and $D_{H\text{-}Cl}$**

There have been several investigations in the literature, as previously reviewed, on the effect of moisture on chloride diffusion in concrete and the results have shown that chloride ingress in concrete is strongly affected by moisture variation. This has been particularly confirmed by the experimental studies conducted by Abarr (2005) and Nagesh and Bhattacharjee (1998) that chloride penetration into concrete depends on degree of saturation and moisture gradient. In particular, the rate of chloride transport can be accelerated by a moisture gradient when the two gradients are in the same direction. On the other hands, the chloride flux can be reduced by a moisture gradient when the two gradients are not in the same direction. Another finding from these two studies was that the apparent chloride diffusion coefficient obtained under an unsaturated condition is that the coefficient depends on chloride concentration.

Similarly, it has been found from the experiment conducted by Ababneh and Xi (2002) that the moisture transport in concrete is influenced by chloride transport. Their results indicated that the coupling parameter due to the effect of chloride transport on moisture penetration in concrete is concentration dependent, depending on the concentration of chloride. Because both $D_{Cl\text{-}H}$ and $D_{H\text{-}Cl}$ are chloride concentration dependent, we can use the following simplified models to describe them

$$D_{Cl-H} = \varepsilon Cl_f \tag{57}$$

$$D_{H-Cl} = \delta Cl_f \tag{58}$$

in which ε and δ are two material constants depending on concrete mix design and age of concrete. In order to determine ε and δ, the chloride profiles obtained from the numerical results of coupled chloride and moisture diffusion in concrete are plotted against the test data by Abarr (2005). For a specific concrete at a certain age, the two constants can be estimated by the best curve fitting between test data and numerical results of coupled chloride and moisture transport in concrete. The two material constants were analyzed based on available test data and determined in a previous study, ε = 0.19 and δ = 0.52 (2013).

- **$D_{Cl\text{-}T}$**

The available material model on this parameter developed by Isteita (2009) is used in the present mathematical model. The study was carried out under chloride ponding test with various temperature conditions. The concrete specimens were ponded with 3% NaCl solution on the top surface. The results revealed that when the temperature of the chloride solution is increased, chloride ions penetrate faster from the top to bottom of concrete samples. This means the increasing temperature gradient contributes significantly to chloride penetration. So, under non-isothermal condition, the coupling effect due to the effect of temperature variation on chloride penetration cannot be simply ignored. A model for this coupling parameter was developed by Isteita (2009) using a multi-factor equation taken into account the influential parameters such as free chloride concentration, age of concrete, and temperature given by:

$$D_{Cl-T} = 5\times10^{-8} C_f \, f_1(t) f_2(T) \tag{59}$$

where $f_1(t)$, is the factor considering the age effect of concrete which corresponds to the degree of hydration of concrete:

$$f_1(t) = 4t^{-1} \tag{60}$$

in which *t* represents the age of concrete. The temperature effect is taken into account and given by the second factor, $f_2(T)$. Using the Arrhenius's equation, it is written as:

$$f_2(T) = Exp(0.1\frac{U}{R}(\frac{1}{T_{ref}} - \frac{1}{T})) \tag{61}$$

where *U* is the activation energy of the diffusion process; *R* is the universal gas constant; and *T* and T_{ref} are current and reference temperatures, respectively. It is important to point out that the value 5×10^{-8} in Eq. (59) is only valid for the concrete used in the study by Isteita (2009), and the value will vary when a concrete with a different mix design is to be used.

- **D_{H-T}**

It should be pointed out that the available test data and/or material models regarding the influence of temperature on moisture diffusion in concrete are still very limited. So far, most research has focused on the influence of temperature change on moisture transport in high temperature range but very few publications have considered the moisture-temperature coupling effect in normal temperature. An investigation on the influence of temperature variation on moisture movement for concrete was carried out by Khoshbakht (2009) and a model for the coupling parameter was developed as shown in Eqs. (62) and (63). Due to data scarcity, we used this model as a simple approximation for the coupled effect of temperature variation on moisture diffusion in concrete in the present study.

$$D_{H-T} = \rho_0 \begin{pmatrix} 1.67x10^{-8}\theta^5 - 3.99x10^{-6}\theta^4 + 2.58x10^{-4}\theta^3 \\ -4.14x10^{-3}\theta^2 + 0.216\theta - 0.035 \end{pmatrix} x10^{-3} \tag{62}$$

$$\theta = 226.68H^3 - 247.75H^2 + 123.45H + 0.1076 \tag{63}$$

in which ρ_0 = 2,200 kg/m^3, ϑ is the moisture content, and *H* is relative humidity.

- **D_{T-H} and D_{T-Cl}**

Theoretically, both chloride and moisture transport in concrete have some effects on temperature variation because the mass transports carry heat with them. However, the level of chloride concentration is low and the intensity of moisture transport is small (no liquid flow in good quality concrete), these two coupling effects can be dropped (2009). So, the parameter D_{T-H} and D_{T-Cl} are not included in the governing equations.

4 Results and Discussion

4.1 Numerical simulation for multi-ionic species diffusion in saturated and non-isothermal concrete

Numerical simulations are performed to study the effect of temperature on transport of chloride and others ionic species in saturated concrete and to compare with the available test data. The material models discussed in the previous sections are incorporated in the governing equations, Eqs. (19) and (20). In the present study, the finite element method is employed for solving partial differential equations of ionic transport and the heat conduction in saturated concrete. The numerical study was focused on NaCl penetrating into concrete sample from the top surface of a concrete slab. The ions in concrete pore solution, Na^+, K^+, and OH^-, are considered in the numerical analysis. The material parameters and input data for numerical simulations related to the governing equations are shown in Table 2. This information include diffusion coefficients, initial concentration at the top surface, and initial concentration in concrete pore solution of each ionic species, water-to-cement ratio, and volume fraction of aggregate. The concentration of alkali ions in pore solution, Na^+ and K^+, are obtained from the cement manufacturing company which provided the chemical composition of cement used in the experimental study. The concentration of hydroxyl ion can be calculated by using electroneutrality condition. The numerical simulations were performed under saturated condition. This means that the relative humidity inside and outside concrete sample are equal to 100%. As a result, there is no effect from moisture gradient on multi-ions diffusion in the present study. The units of all ionic concentrations are in mol/l except for the total chloride which is in grams of chloride/gram of concrete weight (g/g) as mentioned in AASHTO T 259 and AASHTO T 260.

The geometry of concrete sample used in numerical simulation is shown in Fig. 5. It is a 3 cm by 5 cm concrete specimen. The concrete sample is exposed to 1 mol/l NaCl solution on the top surface. The other boundaries are assumed to be insulated. The moisture condition inside the concrete sample is assumed to be fully saturated, 100% RH. The concrete sample is divided into 400 elements and 451 nodes by using isoparametric elements for the finite element analysis. In order to compare with available test data, the numerical simulations were conducted in three different cases as shown in Fig. 5. For case 1, 2, and 3, the temperatures on the top surface of concrete samples are 50 ^oC, 35 ^oC, and 20 ^oC, respectively. And, the initial temperature inside specimens is specified as 20 ^oC. This means there is no temperature gradient for case 3.

Table 2 Material parameters and input data

	Cl	Na	K	OH
Diffusion coefficient (m^2/s)	D_{Cl} (Eq. 9)	*$2.7\text{x}10^{-11}$	*$3.9\text{x}10^{-11}$	*$5.28\text{x}10^{-10}$
Initial pore solution concentration (mol/l)	0.0	0.0389	0.0995	0.1384
Heat capacity (J/kg °C)	§1,000			
Thermal diffusivity (W/m °C)	§2			
Chloride binding capacity	dC_f / dC_t (Eqs. 17 and 29)			
Coupling parameter	$D_{i\text{-}T}$ (Eq. 31)			
Water-cement ratio	0.55			
Volume fraction of aggregate	0.65			
Cement type	I/II			

* The values are taken from Wang et al. (2005).

§ The values are taken from Isgor and Razaqpur (2004).

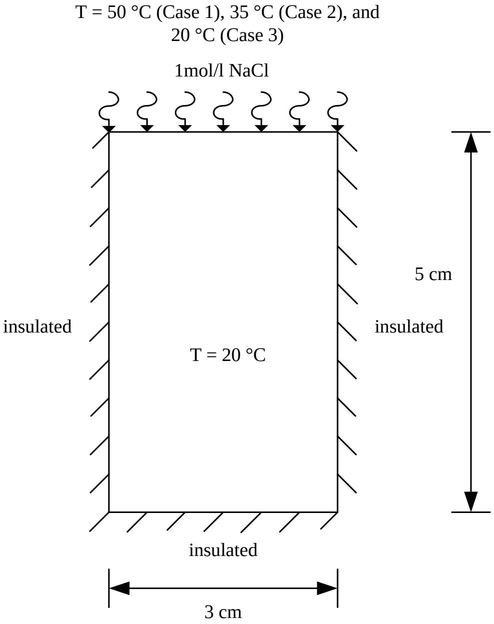


Fig. 5 Geometry and boundary conditions of concrete specimen used for numerical analysis

The concentration profiles of chloride, sodium, potassium, and hydroxyl ions exposed to 1 mol/l NaCl solution at different initial temperature conditions (T = 50 °C, 35 °C, and 20 °C) are shown in Figs. 6, through 17. At T = 50 °C, as shown in Figs. 6 through 9, the concentration of chloride is remarkably influenced by temperature, especially at the depth close to the exposed surface which can be seen as an instant increase from Fig. 6. After this point, the concentration decreases with increasing depth. Fig. 7 shows the concentration profile of sodium which decreases when the depth of penetration increases. It is evident from Figs. 6 and 7 that the concentration gradients of sodium and chloride share the same trend from the top to bottom surface. This is because the initial concentration of these two ions inside the specimen is lower than that at the exposed surface.

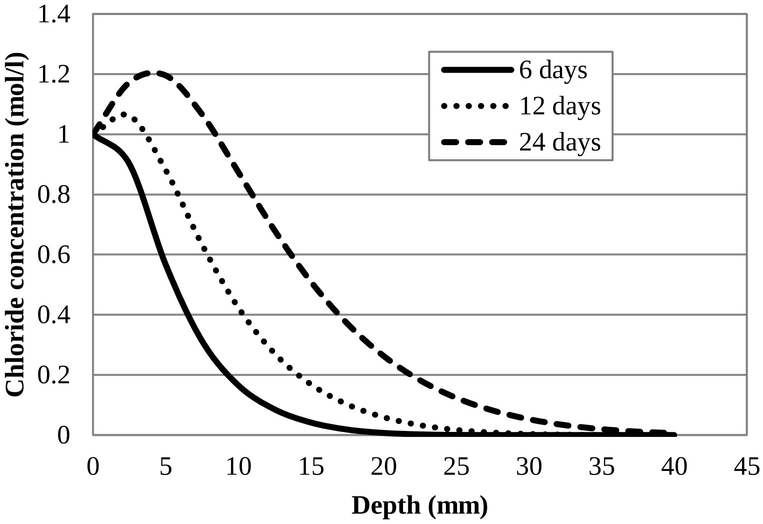


Fig. 6 Chloride concentration profiles at T = 50 °C

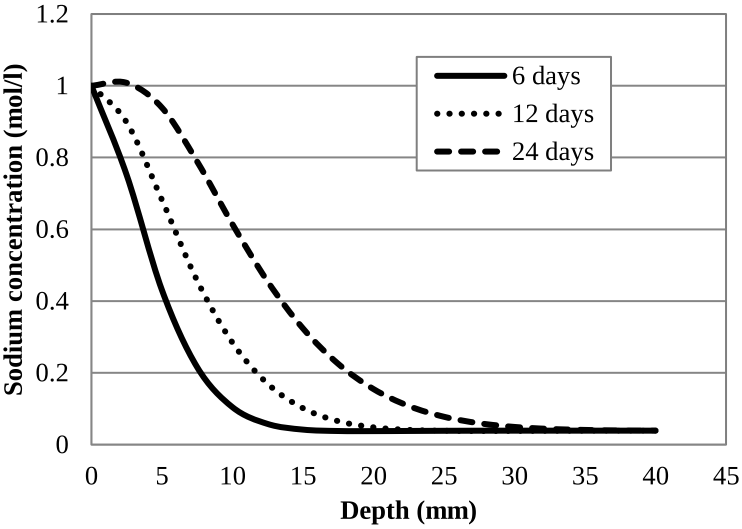


Fig. 7 Sodium concentration profiles at T = 50 °C

For hydroxyl ions, the concentration increases when the depth of penetration increases, as shown in Fig. 8, which is due to the fact that the hydroxyl ions have a lower concentration at the exposed surface than the deep part of the concrete slab. In fact, there are no hydroxyl ions at the top (exposed) surface. The concentration gradient of hydroxyl is in the reverse direction of chloride and sodium ions. The distribution profile of potassium starts from zero at the exposed surface, similar to hydroxyl ions, and increases until reaching the peak, as shown in Fig. 9, which is the point adjacent to the exposed surface and then drops to the initial value of pore solution concentration. The main reason for this reversal (increase and then decrease) is due to the electroneutrality condition in which the negatively charged ions, Cl^- and OH^-, must be balanced by the positively charged ions such as K+.

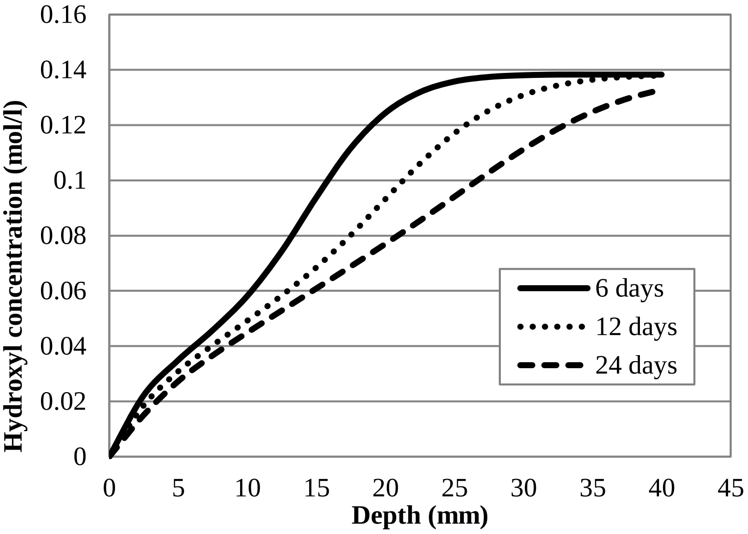


Fig. 8 Hydroxyl concentration profiles at T = 50 °C

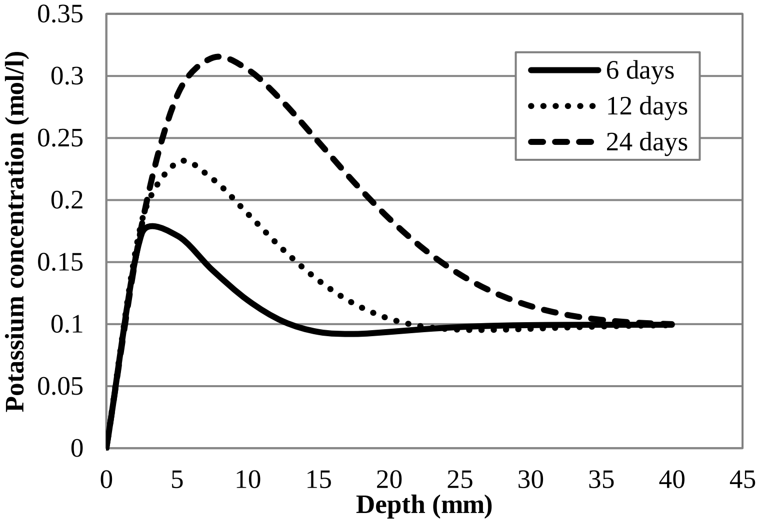


Fig. 9 Potassium concentration profiles at T = 50 °C

At T = 35 °C the coupled temperature effect has less impact than at T = 50 °C because of the lower temperature gradient. As noticed from Figs. 10 and 11, there is no instant increase of chloride and sodium profiles at the depth close to exposed surface. Thus, at T = 35 °C, chloride and sodium concentrations decrease monotonically, while Figs 12 and 13 show that hydroxyl and potassium concentrations increase with increasing depth from exposed surface. Figs. 14 through 17 illustrate the distribution profiles of chloride, sodium, hydroxyl, and potassium ions at T = 20 °C. It can be seen that the concentration profiles of these four ionic species have the same trends as obtained from T = 35 °C. The transport mechanisms of the four ions at T = 20 °C are mainly due to diffusion and migration processes because of no temperature gradient. The relationship between concentration and exposure time of these four ionic species can be observed from Figs. 6 through 17 that, at any fixed depth, the concentrations of chloride and sodium ions are higher with the longer period of exposure whereas the concentrations of potassium and hydroxyl ions tend to decrease with an increase of exposure time.

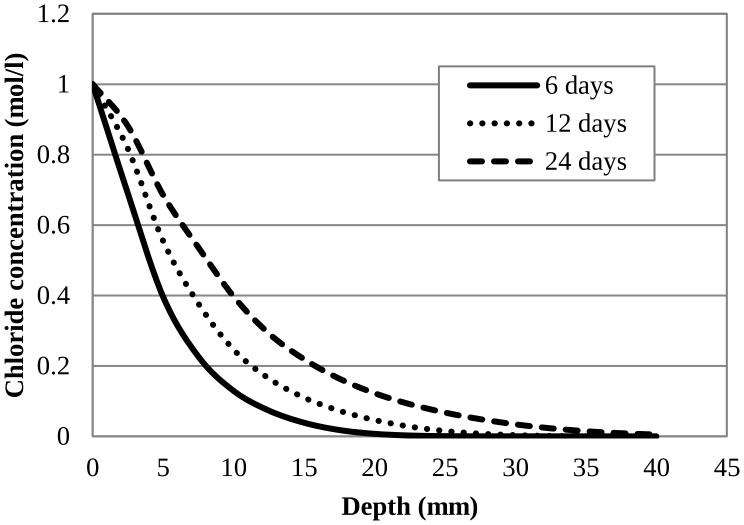


Fig. 10 Chloride concentration profiles at T = 35 °C

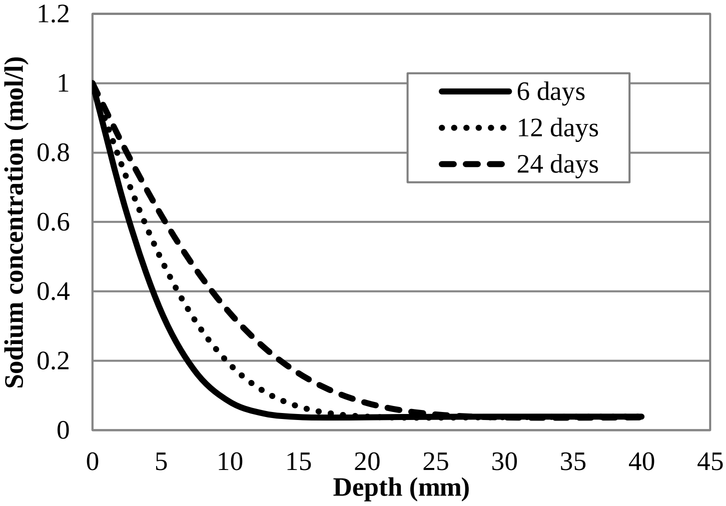


Fig. 11 Sodium concentration profiles at T = 35 °C

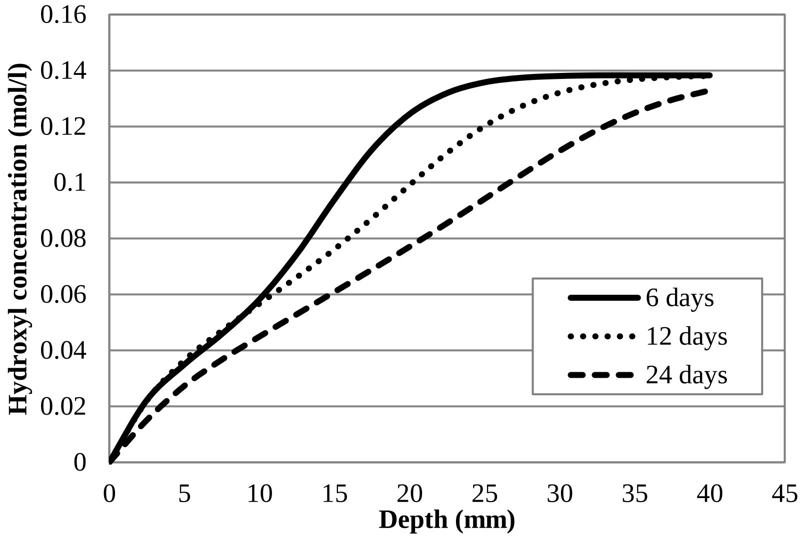


Fig. 12 Hydroxyl concentration profiles at T = 35 °C

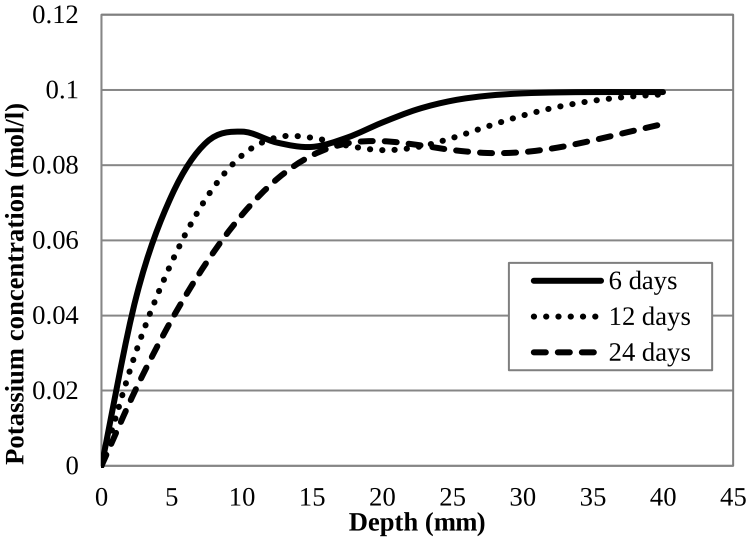


Fig. 13 Potassium concentration profiles at T = 35 °C

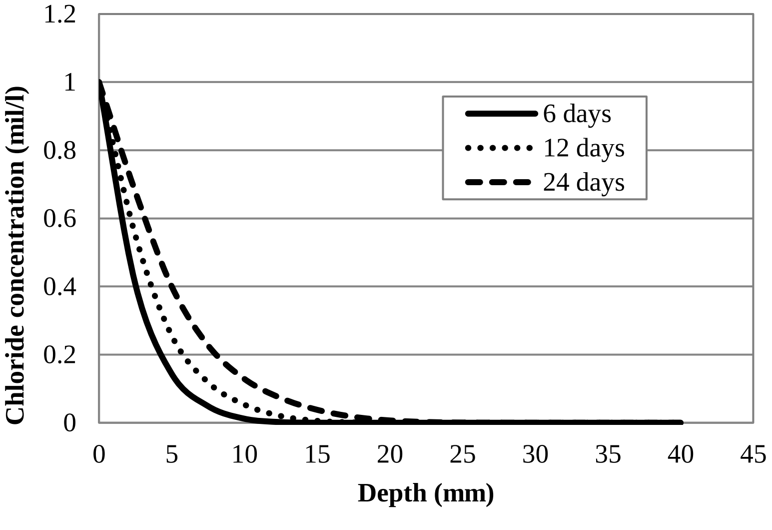


Fig. 14 Chloride concentration profiles at T = 20 °C

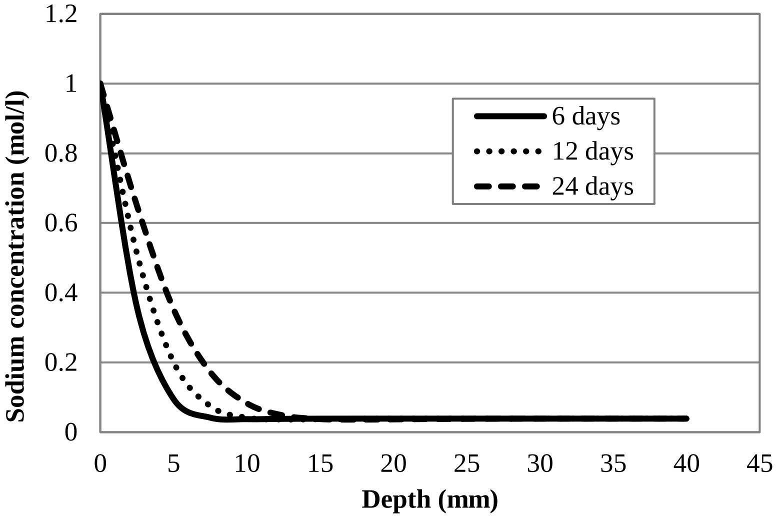


Fig. 15 Sodium concentration profiles at T = 20 °C

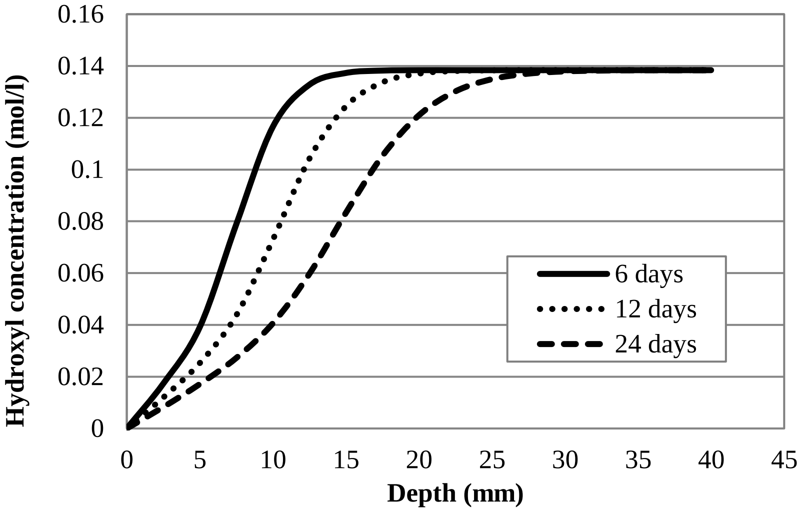


Fig. 16 Hydroxyl concentration profiles at T = 20 °C

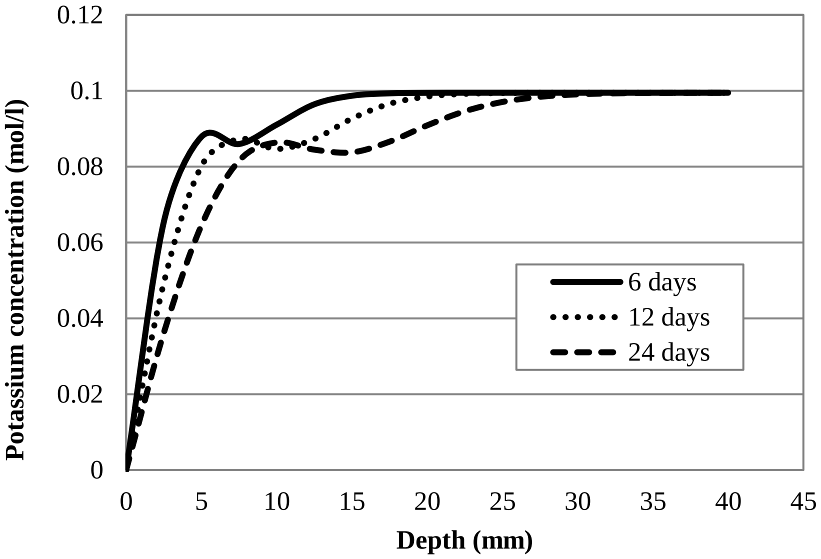


Fig. 17 Potassium concentration profiles at T = 20 °C

Figs. 18 through 29 show the influence of temperature on ionic diffusion at different times of exposure (6, 12, and 24 days of exposure). One can see from these plots that the variations of concentration profiles of the four ionic species can be observed with increasing temperature. The higher the temperature gradient, the more significant of the coupled temperature effect. At 6, 12, and 24 days of exposure, with increasing temperature, the concentration of chloride and sodium ions increase, at any fixed depth, which is accelerated by temperature gradient. Moreover, at T = 50 °C, at any times of exposure, chloride and sodium ions are accelerated by higher temperature gradient when compared with T = 35 °C. Therefore, At T= 50 °C, hydroxyl ion diffuses faster to satisfy the electroneutrality condition with positively charged ions, Na^+ and K^+. From Figs. 20 and 28, hydroxyl concentration at T = 50 °C is slightly higher than at T = 20 °C at the depth close to the exposed surface due to the electroneutrality condition. With increasing depth from this area, hydroxyl concentration at T = 20 °C is higher than both at T = 50 °C and 35 °C because the diffusion rate of hydroxyl ion is slowed down by temperature gradient. For potassium ions, when temperature increases from 20 °C to 35 °C the concentration at higher temperature is lower than at the lower temperature, at any times of exposure. This is mainly due to the heat flux which is in the reverse direction of concentration gradient of potassium so that the diffusion rate of potassium is actually reduced by the temperature gradient. However, when temperature reaches T = 50 °C the concentration is higher than at T = 35 °C and 20 °C. This is because at this temperature range, the transport mechanism of potassium is dominated by the electroneutrality condition. As noticed from numerical results, we can conclude that the concentrations of four ionic species are significantly influenced by temperature variation.

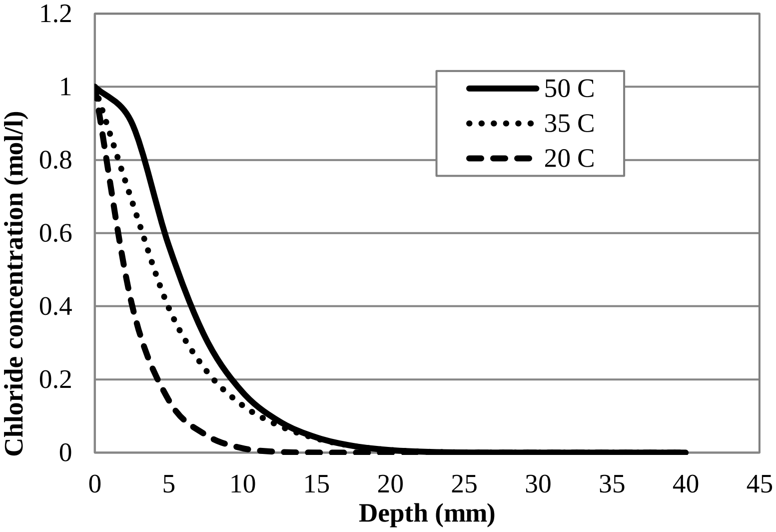


Fig. 18 Chloride concentration profiles exposed to 1 mol/l NaCl solution at 6 days

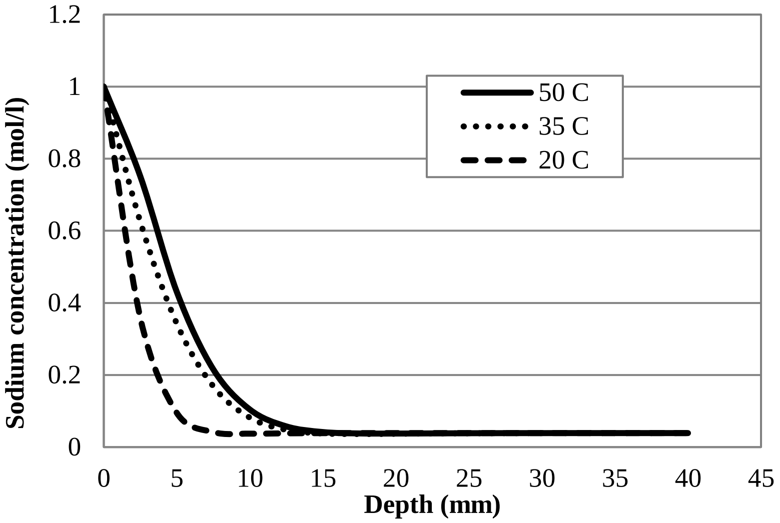


Fig. 19 Sodium concentration profiles exposed to 1 mol/l NaCl solution at 6 days

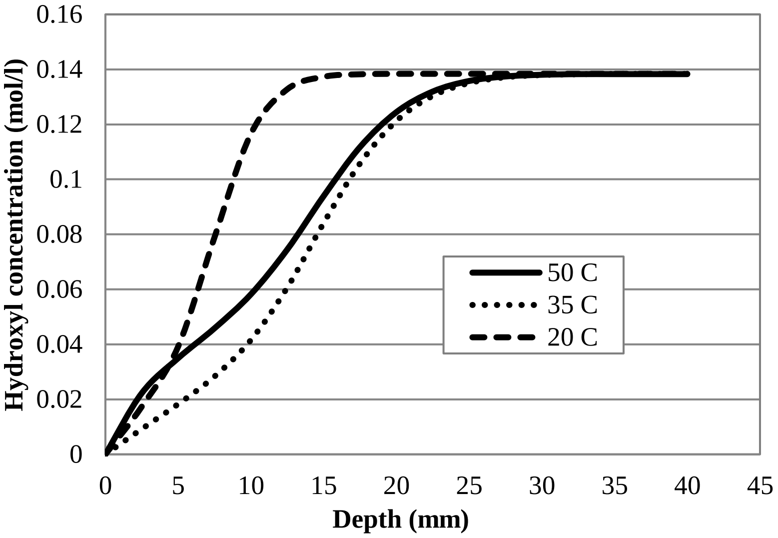


Fig. 20 Hydroxyl concentration profiles exposed to 1 mol/l NaCl solution at 6 days

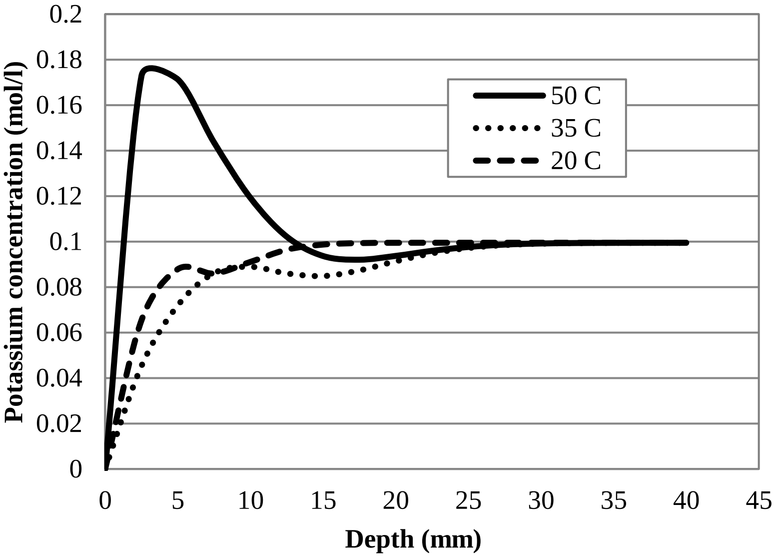


Fig. 21 Potassium concentration profiles exposed to 1 mol/l NaCl solution at 6 days

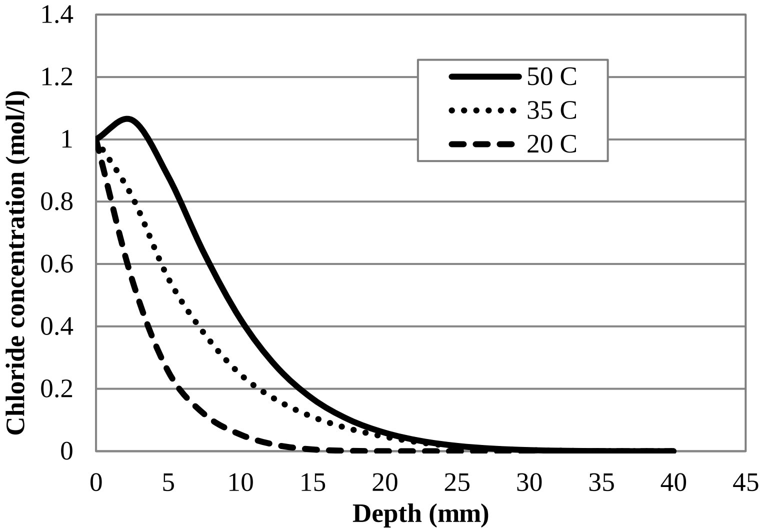


Fig. 22 Chloride concentration profiles exposed to 1 mol/l NaCl solution at 12 days

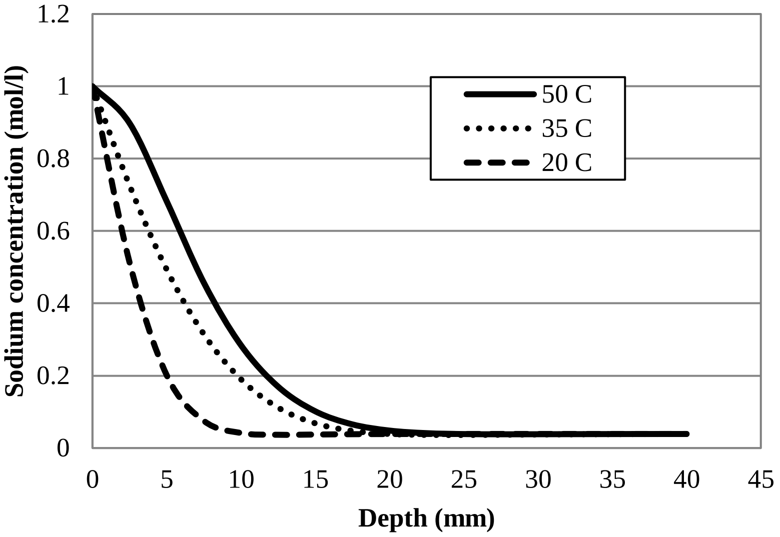


Fig. 23 Sodium concentration profiles exposed to 1 mol/l NaCl solution at 12 days

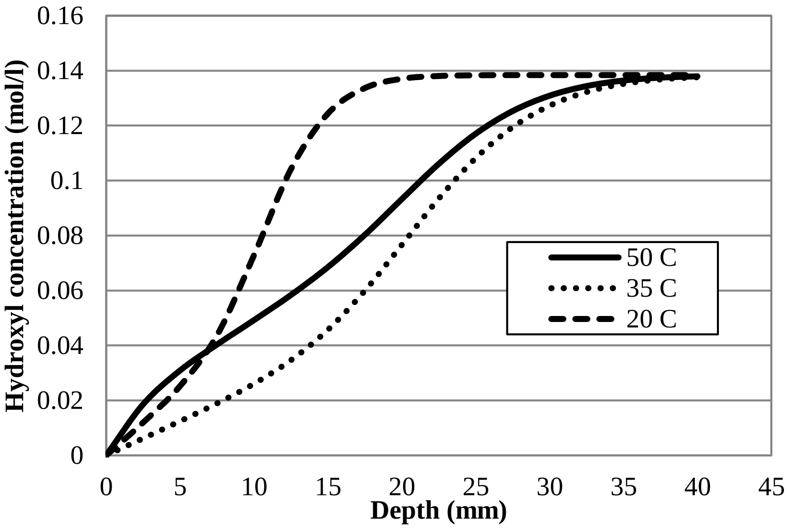


Fig. 24 Hydroxyl concentration profiles exposed to 1 mol/l NaCl solution at 12 days

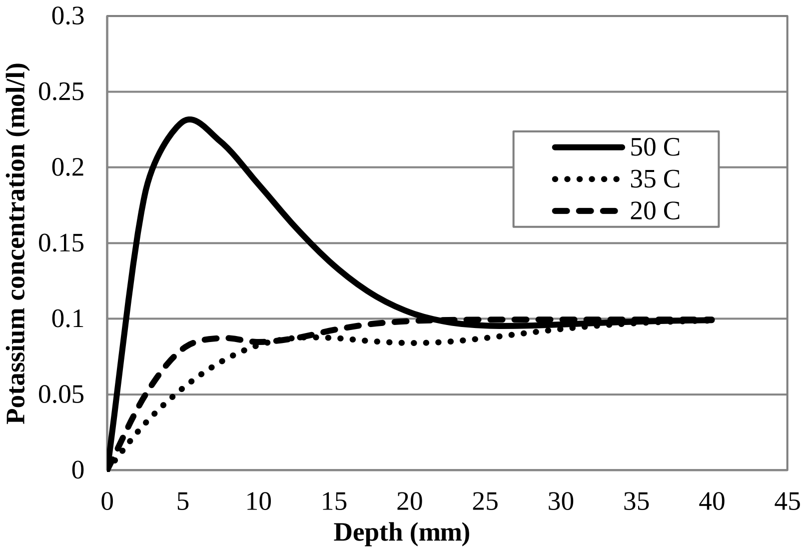


Fig. 25 Potassium concentration profiles exposed to 1 mol/l NaCl solution at 12 days

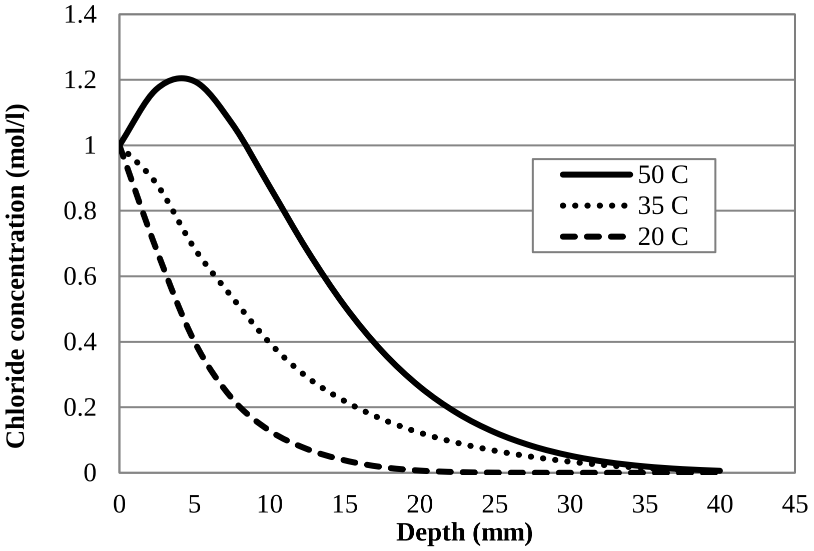


Fig. 26 Chloride concentration profiles exposed to 1 mol/l NaCl solution at 24 days

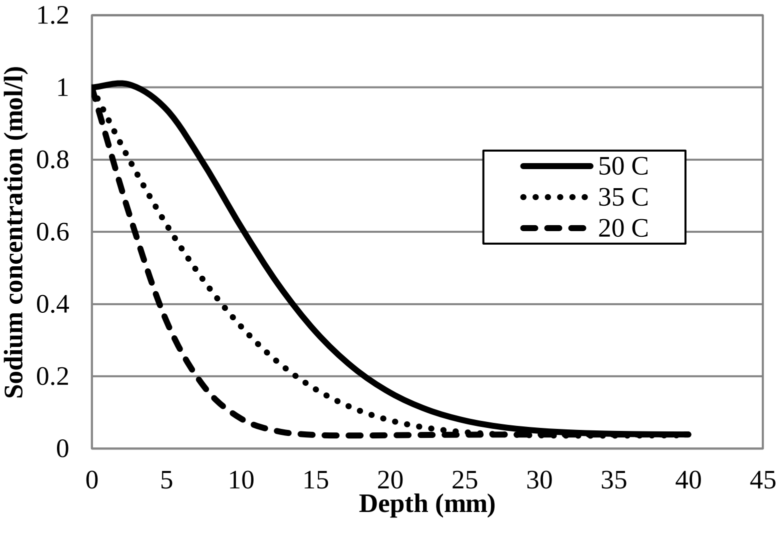


Fig. 27 Sodium concentration profiles exposed to 1 mol/l NaCl solution at 24 days

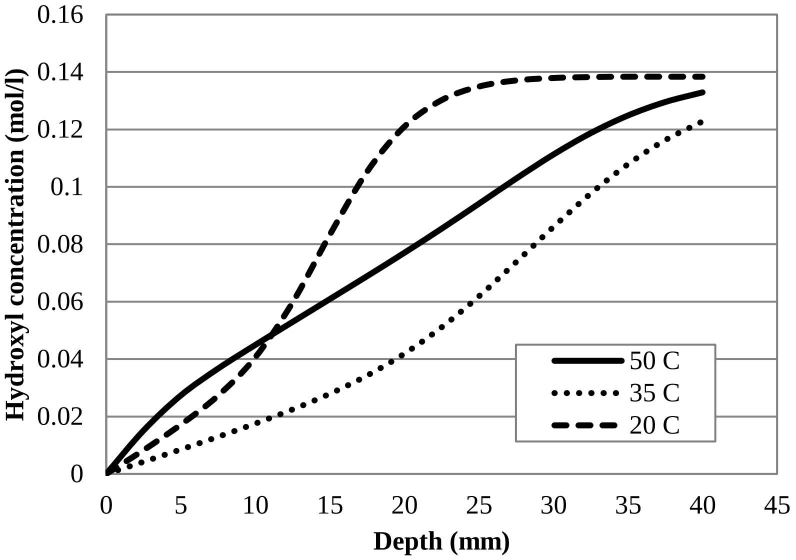


Fig. 28 Hydroxyl concentration profiles exposed to 1 mol/l NaCl solution at 24 days

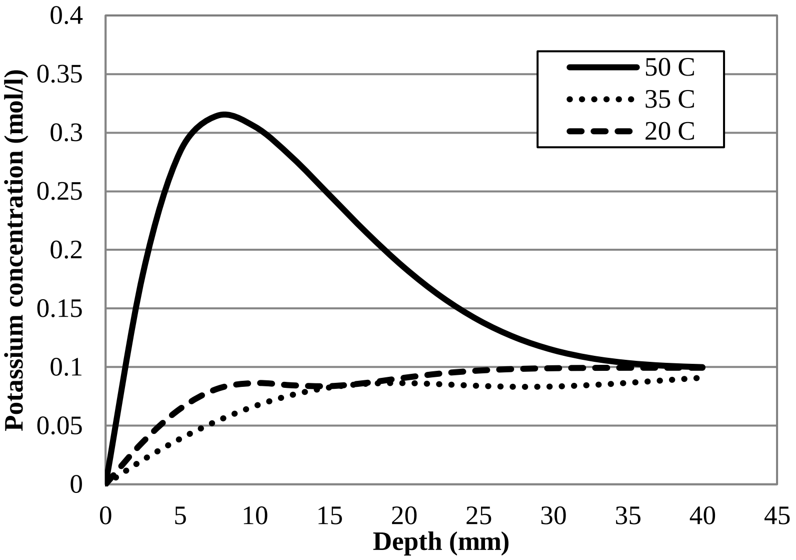


Fig. 29 Potassium concentration profiles exposed to 1 mol/l NaCl solution at 24 days

- **Comparison with test data**

The results of total chloride concentration (in gram of chloride per gram of concrete) predicted by the present model are plotted and compared with the available test data obtained from Isteita (2009). The chloride ponding tests were conducted at different initial temperature conditions at the exposed (top) surface. The comparisons between numerical and experimental results exposed to 3% NaCl at T = 50 °C for 6 and 12 days of exposure are shown in Figs. 30 and 31, respectively. Figs. 32 and 33 present the comparisons at T = 35 °C for specimens exposed to 3% NaCl for 6 and 12 days of exposure, respectively. It can be seen from Figs 30 through 33, at T = 50 °C and T = 35 °C, that the results obtained from the present model have a good agreement with test data. Therefore, the present comprehensive model taking into account the diffusion mechanisms, ionic interaction, and the coupled temperature effect can be used to predict the chloride penetration into concrete structures not only in isothermal condition but also in non-isothermal condition.

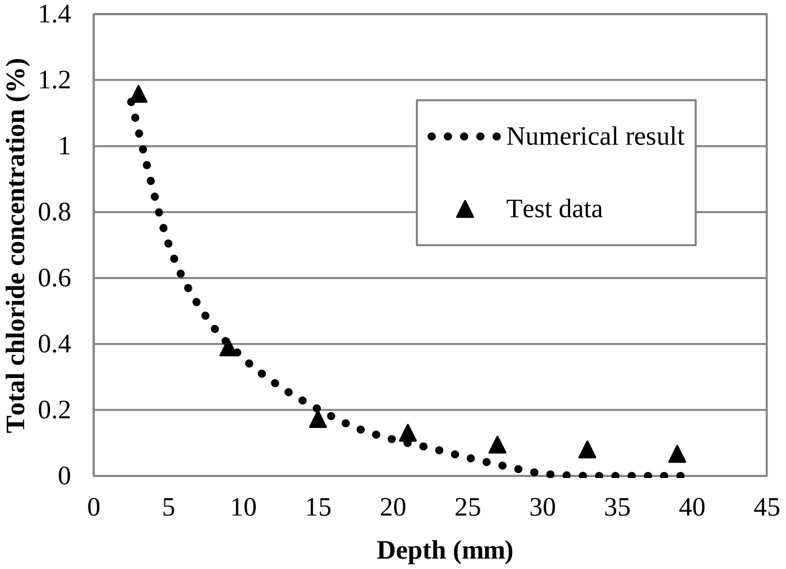


Fig. 30 The comparison between numerical result and test data at 6 days of specimens exposed to T = 50 °C

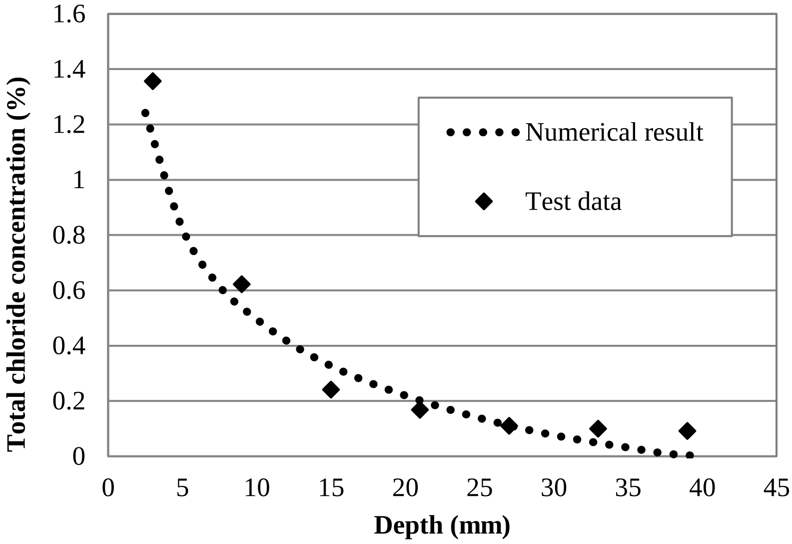


Fig. 31 The comparison between numerical result and test data at 12 days of specimens exposed to T = 50 °C

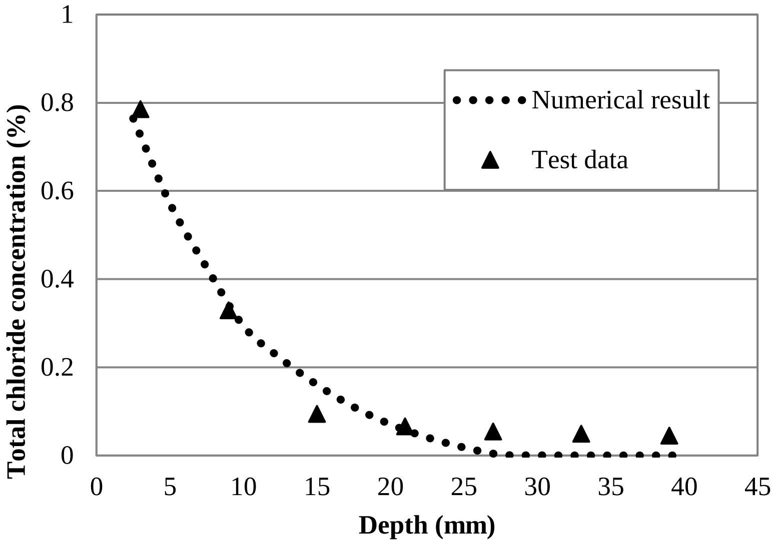


Fig. 32 The comparison between numerical result and test data at 6 days of specimens exposed to T = 35 °C

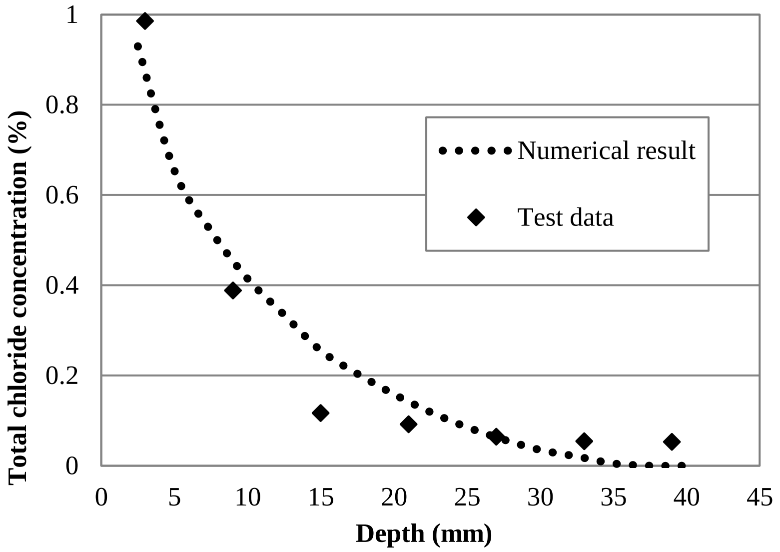


Fig. 33 The comparison between numerical result and test data at 12 days of specimens exposed to T = 35 °C

4.2 Numerical simulation for multi-ionic species diffusion in non-saturated and non-isothermal concrete

A concrete specimen with 3 cm by 5 cm, as shown in Fig. 34, is numerically analyzed using the finite element method. The sample is exposed to 1 mol/l NaCl solution and, at the top surface, the relative humidity and temperature are initially specified as 100% RH and 35 ^{o}C, respectively. The inside relative humidity and temperature are given as 50% RH and 20 ^{o}C, respectively. The other boundaries are assumed to be sealed without any exchange of moisture, chloride, and heat. The defined material parameters and input data for the numerical analysis related to the governing equations are shown in Table 3.

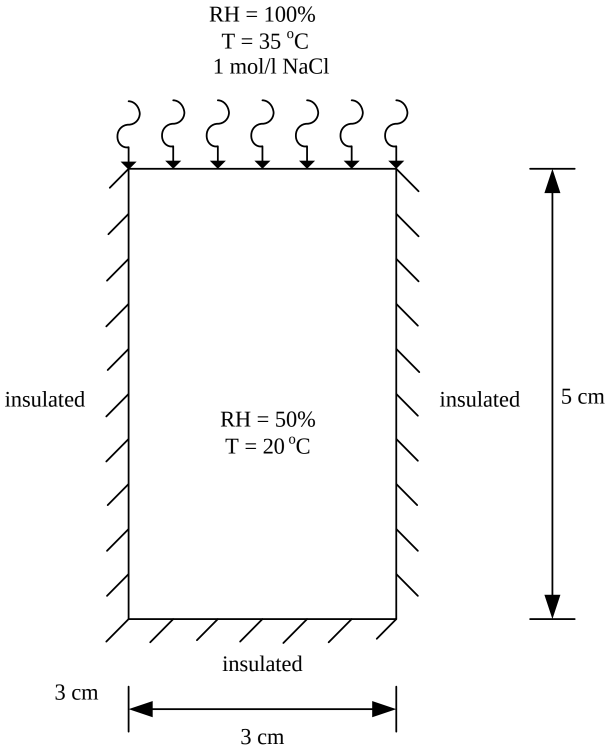


Fig. 34 Concrete sample used in the numerical simulation

Table 3 Material parameters and input data for simulated concrete specimen

Parameter	Value
Water to Cement Ratio, w/c	0.55
Volume Fraction of Aggregate, g_i	0.65
Cement type	I
Curing time (days)	28
Heat capacity, $\partial Q/\partial T$ (J/kg °K)	*1,000
Thermal diffusivity, D_T (W/m °K)	*2

* The values are taken from Burkan Isgor and Razaqpur (2004).

Figs. 35, 36, and 37 demonstrate moisture profiles of concrete samples at 10, 50, and 100 days of exposure, respectively. As seen from these figures, at any fixed depth, pore relative humidity of non-saturated concrete is lower than the saturated condition. When the temperature effect is considered, the moisture level at any fixed depth is higher than that without the temperature effect because the moisture transport is accelerated by the temperature gradient. This effect is less significant at 100 days of exposure because the concrete becomes saturated. Fig. 38 shows the distribution profiles of free chloride concentration at different times of exposure at non-saturated and non-isothermal conditions. The initial chloride concentration inside concrete sample is assumed to be zero so that chloride ions penetrate from outside (top surface) to inside specimen. This can be noticed from Fig. 38 that the free chloride concentration decreases with increasing depth from the top surface. The trends also illustrate that, at any depth, the free chloride concentration is higher when exposure time is longer.

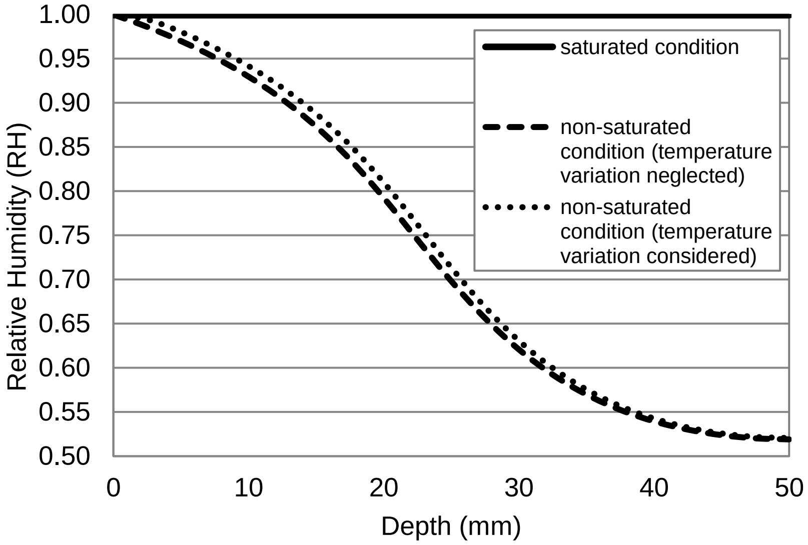


Fig. 35 Moisture profiles at 10 days of exposure

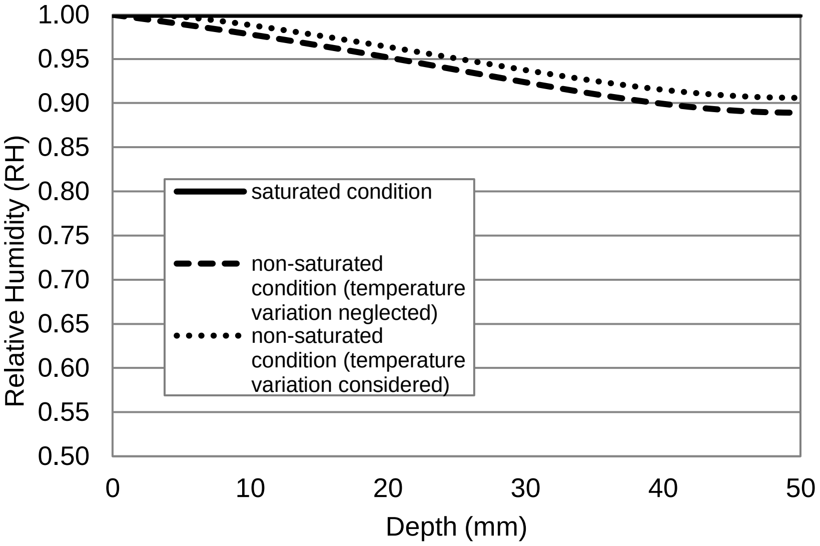


Fig. 36 Moisture profiles at 50 days of exposure

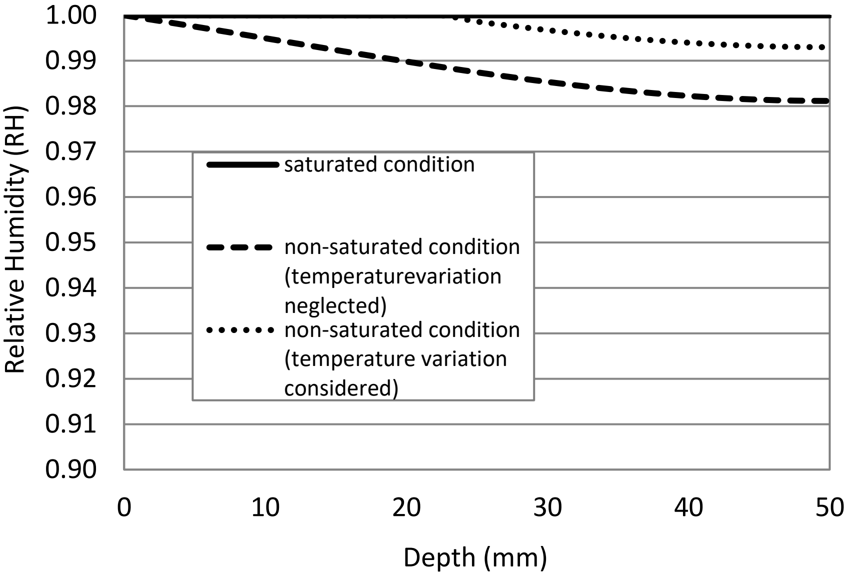


Fig. 37 Moisture profiles at 100 days of exposure

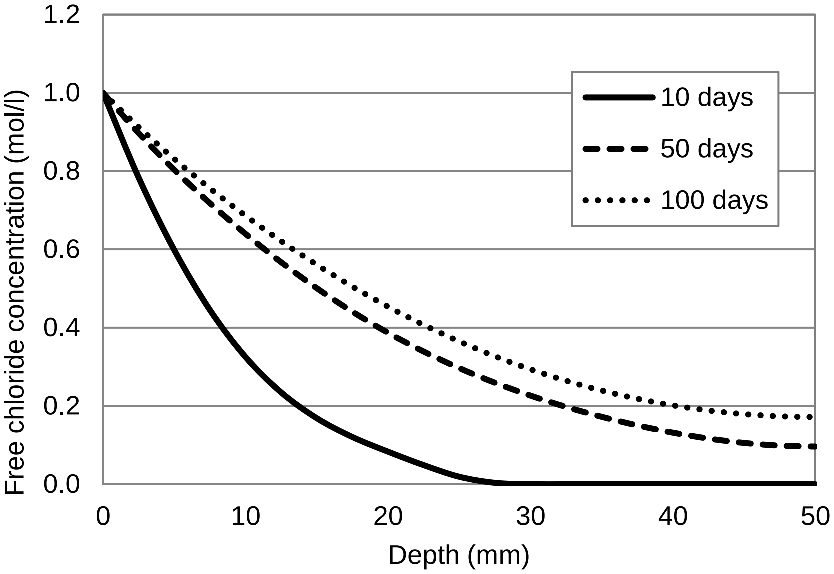


Fig. 38 Free chloride concentration profiles at different times of exposure

Free chloride concentration is plotted against the depth from the top surface at 10, 50, and 100 days of exposure are shown in Figs. 39, 40, and 41, respectively. As observed from these figures, at any fixed depth, the chloride concentration at non-saturated condition is higher than saturated state. This is because, as explained earlier, the chloride penetration is accelerated by the moisture penetration when they are in the same direction. Figs. 39, 40, and 41 also show that when the temperature variation is taken into account, the change of chloride concentration can be apparently observed. Heat flow can accelerate the diffusion rate of both moisture and chloride. As mentioned previously, moisture diffusion can carry chloride ions so that, with increasing rate of moisture transport due to the temperature effect, chloride ions can ingress faster leading to higher concentration. Thus, from chloride concentration profiles as shown in Figs 39 through 41, it can be concluded that the coupled effects of temperature variation and moisture transport on chloride diffusion in concrete are very significant and they cannot be negligible. The present model takes into account the coupling parameters very well and the model can be used to simulate chloride transport in concrete structures which is frequently found in non-saturated and non-isothermal condition.

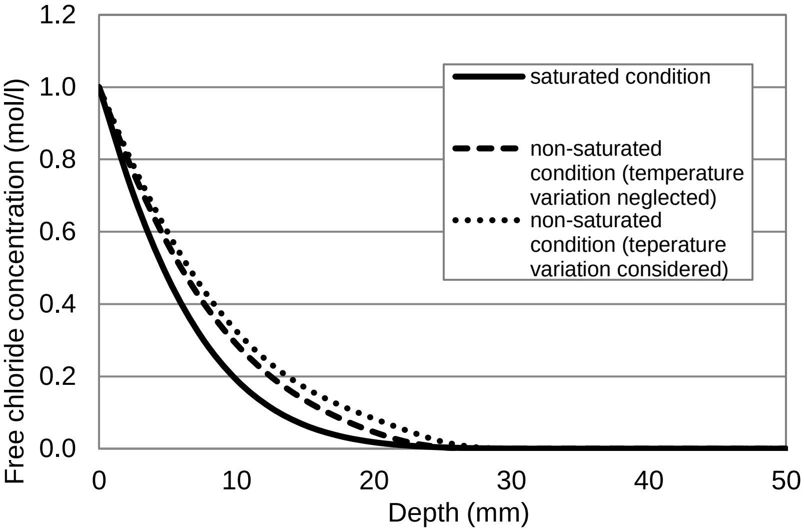


Fig. 39 Free chloride concentration profiles at 10 days of exposure

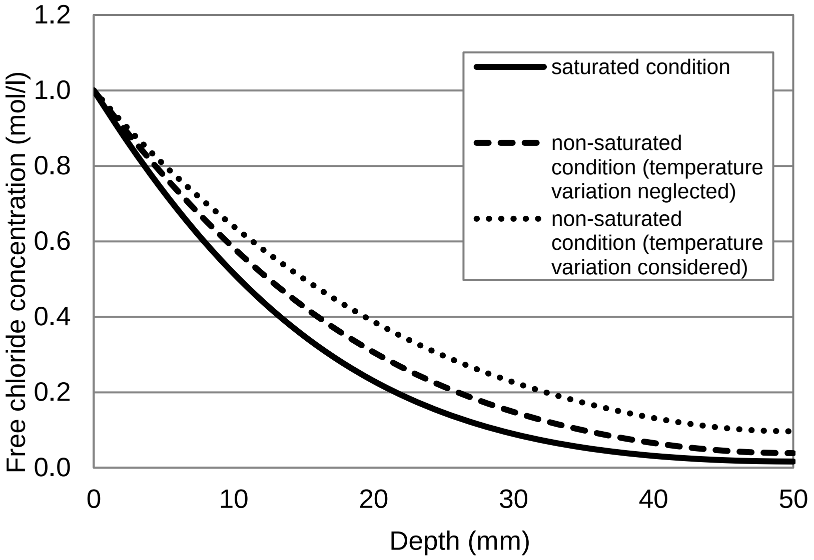


Fig. 40 Free chloride concentration profiles at 50 days of exposure

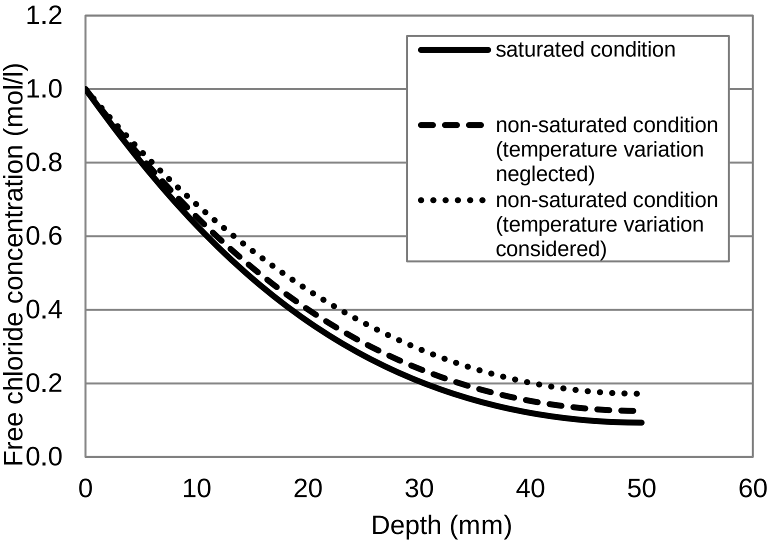


Fig. 41 Free chloride concentration profiles at 100 days of exposure

Due to the lack of systematic test data in the literature on chloride diffusion in non-saturated and non-isothermal condition, we compare the present numerical results to available experimental data which were conducted using chloride ponding test in 1) non-saturated and isothermal condition and 2) saturated and non-isothermal condition.

Fig. 42 shows the comparison between numerical results obtained from the present model and the test data conducted on chloride ponding test at 90 days of exposure by Andrade and Whiting (1996). The experiment was performed on concrete with two different water cement ratios, w/c = 0.4 and 0.6. The concrete samples were kept in non-saturated and isothermal condition. As illustrated from Fig. 42, a good agreement is observed. Figs. 43 and 44 demonstrate the verification of the proposed model with test results of chloride ponding test on concrete in non-isothermal and saturated condition. The concrete sample was exposed to 3% NaCl solution at the top surface. The experiments were carried out at 6 and 12 days of exposure with the controlled temperature at the exposed (top) surface, T = 35 ^{o}C. The temperature inside specimens was maintained at T = 20 ^{o}C. It can be seen from Figs. 10 and 11 that the present model is satisfactory to predict chloride ingress into non-isothermal and saturated concrete. Based on the present comparative studies, it may be concluded that the present mathematical model can be used to adequately predict chloride penetration in non-saturated and isothermal; and non-isothermal and saturated concrete structures.

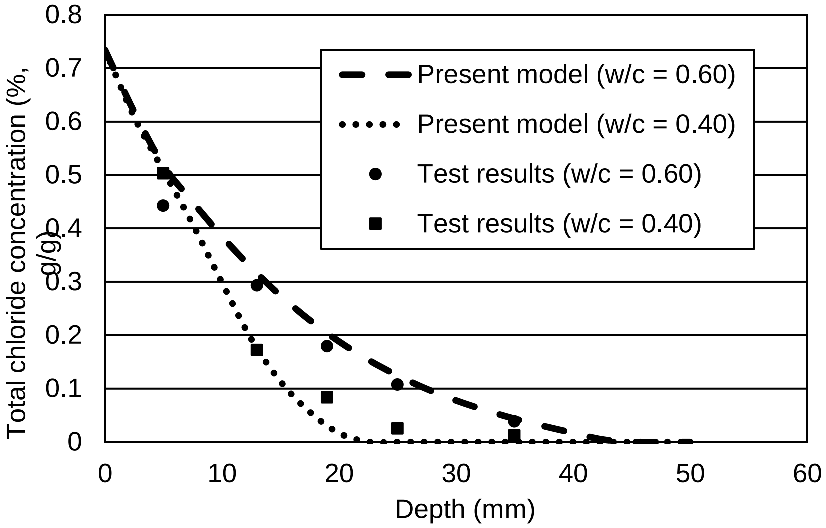


Fig. 42 A comparison between numerical results and experimental data

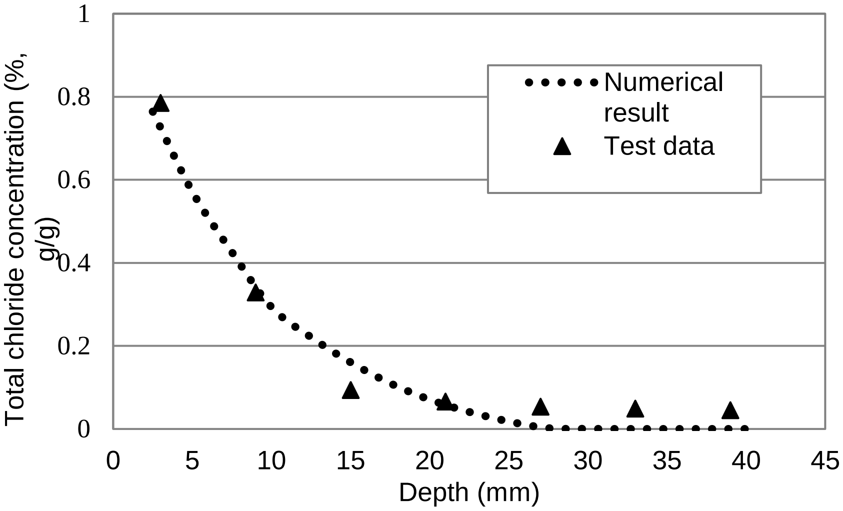


Fig. 43 A comparison between numerical result and test data at 6 days of a specimen exposed to T = 35 °C

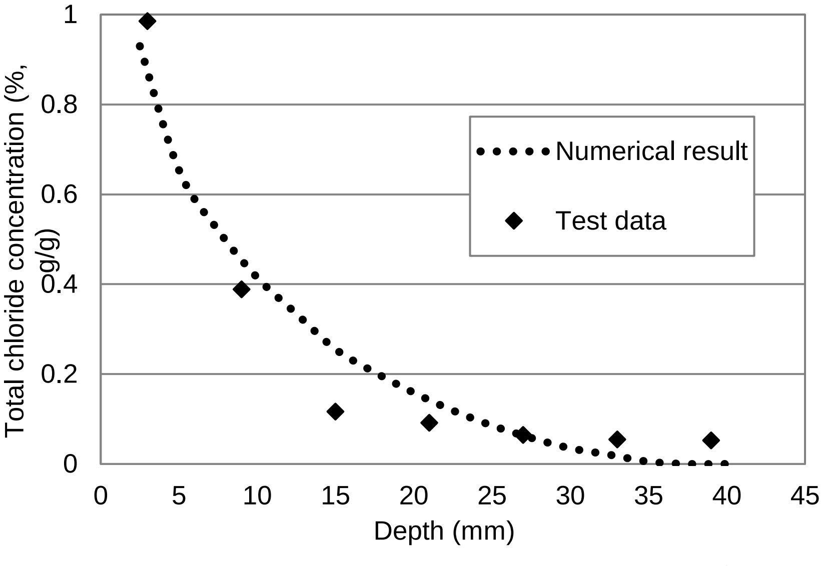


Fig. 44 A comparison between numerical result and test data at 12 days of a specimen exposed to T = 35 °C

5 Conclusion

5.1 Multi-ionic species diffusion in saturated and non-isothermal concrete

- A mathematical model is developed for predicting the chloride penetration into saturated concrete structures under non-isothermal condition. The model takes into account diffusion mechanism due to ionic concentration gradient and migration processes due to ionic interaction of chloride ions and other chemical species in concrete pore solution (Na^+, K^+, and OH^-) which is described by the Nernst-Planck equation.
- The heat flow in concrete is considered in this study which is described by Fourier's heat conduction equation. A coupling term obtained from available test data is proposed. Then, the ionic flux equations are modified by incorporating explicitly the coupling term for the temperature effect. The numerical simulations are performed by assuming a concrete sample exposed to chloride solution (NaCl) at different initial temperature conditions. The governing equations are solved by using the finite element method.
- Material models for the transport parameters were included in the numerical simulation. The diffusion coefficients and the chloride binding capacity were obtained from literature, and the coupling parameters for the temperature effect were developed based on available test data.
- The numerical results show that the coupling term contributes significantly to the diffusion mechanism of four ionic species (Cl^-, Na^+, K^+, and OH^-) by accelerating the penetration rate of chloride and sodium concentration. However, potassium and hydroxyl concentration profiles vary by the temperature effect and electroneutrality condition.
- The numerical results predicted by the present model are validated with the available test data. The comparison shows that the total chloride profiles obtained from the model have a good agreement with the test data.
- The present comprehensive model can be used to predict the chloride ingress into saturated concrete structures under both isothermal and non-isothermal conditions.

5.2 Multi-ionic species diffusion in non-saturated and non-isothermal concrete

- A mathematical model for predicting chloride ingress into concrete is developed based on Fick's law. The model takes into account the fully coupled effect among chloride, moisture, and heat transport. The governing equations are established by including additional terms in the flux equations. The additional terms are explicitly related to the concentration gradients of the state variables, i.e., free chloride concentration, pore relative humidity, and temperature.

- The material models developed for the transport parameters of chloride and moisture diffusion in concrete are introduced. These parameters include chloride diffusion coefficient, chloride binding capacity, moisture diffusivity, and moisture capacity. Some of these parameters are taken into account the factors affecting concrete mix design such as water cement ratio, curing time, and type of cement.
- The proposed coupling parameters between chloride and moisture transport are characterized based on available experimental data. These parameters are not constant but expressed in terms of chloride content dependent. And, the material parameters accounted for the influence of temperature variation on chloride and moisture diffusion are obtained from available material models.
- Finite element numerical simulation model are developed and the model demonstrates that temperature variation has a remarkable influence on moisture and chloride distribution profiles. In non-saturated concrete, chloride penetration is accelerated by moisture movement when the two gradients are in the same direction.
- For non-saturated concrete under non-isothermal condition, chloride flux profiles at any exposure times are significantly influenced by variations in moisture diffusion and heat transfer. These examples exhibit the strong-coupling effect of not only moisture but also heat transfer on chloride transport mechanism. The chloride penetration is accelerated by the heat flow when the two gradients are in the same direction.
- Compared to other models which use Fick's second law and combine all coupling effects into one parameter, i.e. the apparent chloride diffusivity, the present model has explicit and distinct term in each of the governing equations to reflect the effect of each coupling process. Therefore, the present model is a significant improvement in the aspect of modifying the governing equations of chloride, moisture, and heat by incorporating the coupling parameters.
- The present model is validated by comparing the numerical results with the available chloride ponding test data obtained in two separated tests. One is under non-saturated and isothermal condition, and the other is under non-isothermal but saturated condition. Good agreement is satisfactorily obtained.
- There is a lack of experimental data for chloride penetration into concrete under fully coupled non-saturated and non-isothermal condition. Future work is needed to further improve this model by verifying the numerical results with the experimental data with the fully coupled condition.

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6 Output

6.1 International Journal Publication

1) **Damrongwiriyanupap, N.**, Scheiner, S., Pichler, B., and Hellmich, C. (2016) "Self-consistent channel approach for upscaling chloride diffusivity in cement pastes." *Transport in Porous Media*, under revision (the revised paper has been submitted). (Impact Factor = 1.653)
2) Hanjitsuwan, S., Phoo-Ngernkham, T., and **Damrongwiriyanupap, N.** (2016) "Comparative Study using Portland Cement and Calcium Carbide Residual as a Promoter in Bottom Ash Geopolymer." *Construction and Building Materials*, tentatively accepted for publication. (Impact Factor = 2.421)
3) Phoo-Ngernkham, T. Hanjitsuwan, S., **Damrongwiriyanupap, N.**, and Chindaprasirt, P. (2016) "Effect of sodium hydroxide and sodium silicate solutions on strength of alkali activated high calcium fly ash containing Portland cement." *KSCE Journal of Engineering*, In press, doi:10.1007/s12205-016-0327-6. (Impact Factor = 0.600)
4) Kroehong, W., **Damrongwiriyanupap, N.**, Sinsiri, T., Jaturapitakkul, C., and Chindaprasirt, P. (2015) "The effect of palm oil fuel ash as a supplementary cementitious material on chloride penetration and microstructure of blended cement paste.", *Arabian Journal for Science and Engineering*, DOI:10.1007/s13369-016-2143-1. (Impact Factor = 0.728)
5) **Damrongwiriyanupap, N.**, Li, L., Limkatanyu, S., and Xi, Y. (2015) "A Thermo-Hygro-Coupled Model for Chloride Penetration in Concrete Structures.", *Advances in Materials Science and Engineering,* Volume 2015, Article ID 682940, 1-10. (Impact Factor = 1.010)
6) **Damrongwiriyanupap, N.**, Li, L., Limkatanyu, S., and Xi, Y. (2014) "Temperature Effect on Multi-Ionic Species Diffusion in Saturated Concrete.", *Computers and Concrete*, 13(2), 149-171. (Impact Factor = 0.849)

6.2 International Conference

1) **Damrongwiriyanupap, N.**, Scheiner, S., Pichler, B., and Hellmich, C. (2016), Self-consistent chloride diffusivity upscaling in cement paste, Proceedings of the 9th International Conference on Fracture Mechanics of Concrete and Concrete Structures (FraMCoS-9), May 29 – June 1, Berkeley, California, USA.