Sensitivity Analyses on Chloride Ion Penetration into Undersea Tunnel Concrete

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Abstract

The penetration of chloride ion leads to the corrosion initiation in reinforced concrete, which results in decreasing the durability of concrete. A theoretical diffusion-convection model describing the process of chloride ion penetration into concrete under external water pressure is described by considering multiple affecting factors such as unsaturated flow, fluid-solid coupling, and chloride binding. A numerical model of unsaturated concrete is built to simulate the coupled process. Based on this model, the classic expression of effective diffusion coefficient is modified by considering constrictivity factor, and the sensitivity analysis is carried out on five sets of parameters (i.e., effective diffusion coefficient, saturated permeability, van Genuchten parameters, initial saturation, and binding capacity parameters) aiming at evaluating the robustness of the model. The simulation results show that the multi-mechanism penetration model is computationally feasible, and the multiphysics coupling model can well reproduce the chloride ion transfer process in a microscopic perspective. Furthermore, the sensitivity analysis results indicate that the parameters governing moisture transport process are more sensitive to the prediction of the chloride ion penetration into undersea tunnel concrete.

1. Introduction

Concrete is mostly used in engineering for its high compressive strength and relatively low cost. Since deterioration of concrete members is induced and accelerated mainly by chemical agents, the ingress and transportation of those agents are predicted as main indices for durability performance (Yokota and Hashimoto 2013). Simultaneously, the characteristic of porosity and high heterogeneity creates conditions for the invasion of water and external aggressive ion dissolved in water, which reduces the durability of concrete structures. Chloride ion is one of the factors to degrade a reinforced concrete structure. Chloride ion induces the de-passivation of steel reinforcement in concrete and accelerates the corrosion process. Chloride ion penetration into concrete is considered with different mechanisms such as free diffusion driven by concentration gradient, permeation driven by osmotic pressure, migration driven by electrical field, and capillary adsorption driven by surface tension in the capillary pores (Wang et al. 2016). Fick’s second law depicts the process of chloride ion penetration into concrete by diffusion. On the other hand, evidences have indicated that chloride penetration into concrete is a rather complicated process, which is always a combination of different mechanisms depending on the boundary conditions, the moisture state and properties of concrete.

The external environment and internal condition of concrete play important roles on the performance of chloride ion penetration into concrete. The combination of moisture transport and ion transfer is often used to describe the penetration process. Fluid-solid coupling is an interdisciplinary subject related to fluid dynamics and structural dynamics. One kind of coupling between fluids and solids results from direct interaction in pores between fluids and solids of porous medium, which changes in pore-space (mechanical to fluid) and/or in effective stress (fluid to mechanical) (Bouitt et al. 2007). Concrete is an artificial stone made up of cementitious materials, granular aggregates (also known as aggregates), water, and admixtures in a certain proportion added if necessary. Concrete is a kind of porous medium. When the pressure fluid flows through concrete, the coupling between hydraulic process and mechanical process occurs. Dadashi et al. (2017) applied fluid-solid coupling to investigate the safety of the reinforced concrete lining under high internal water pressures. The fluid-solid coupling was used to explain the phenomenon of moisture transport in concrete under water pressure in this paper. A diffusion-convection model was proposed to describe the mechanism of chloride ion penetration into unsaturated concrete by considering many factors such as solution concentration, initial saturation, hydraulic pressure, and water-binder ratio (Saetta et al. 1993; Ababneh et al. 2003; Zhang et al. 2016). Over the past decades, many researchers also investigated chloride ion penetration into concrete driven by capillary absorption and free diffusion (Ababneh et al. 2003; Medeiros and Helene 2009; Otsuki et al. 2003; Wang 2011; Xi and Bazant 1999).
This study aims at investigating the process of chloride ion penetration into concrete in a hydrostatic pressure environment and discussing the sensitivity of input parameters. From the microscopic perspective, the process is described as the diffusion-convective mechanism where the diffusion phenomenon can be influenced by concrete pore structure and the convection is described by the moisture transport in unsaturated concrete. In addition, the authors discuss the coupling of multiple physical fields: the coupling of seepage flow and pore deformation for moisture transport (fluid-solid coupling), as well as the moisture transport field affects chloride ion transfer field. Then, the numerical model is built to solve the partial differential equations and reveals the analysis results. Finally, the sensitivity analysis of parameters is conducted by using the control variates method (i.e., analyzing parameters separately).

2. Theoretical Basis

2.1 Chloride ion transfer

The process of chloride ion penetration into concrete is complicated. Under the external pressure, three basic mechanisms are mixed to govern the transport of ion into unsaturated concrete: binding, diffusion and convection (i.e., driven potential considering both capillary suction and permeation).

It was pointed out by many researchers (Rasheed et al. 1992; Larsen 1998; Tang and Nilsson 1993; Ishida et al. 2008) that the chloride ion shows strong binding affinity with cementitious materials. The aluminate (C₃A) and aluminoferrite (C₄AF) phases in cement have been found to bind with chloride ion chemically, which form Friedel’s salt and calcium chloroferrite. The content of amorphous calcium silicate hydration (CSH) gel in the binder can affect the chloride ion transferred within a porous media by diffusive convection (Martín-Pérez et al. 2001; Bastidas-Artega et al. 2011; Nguyen et al. 2017; Guzmán et al. 2011; Saetta et al. 1993).

The flux of chloride ion transfer in the porous media can be expressed as:

\[ J_{\text{diff}} = -D_e \cdot \nabla C_f + u \cdot C_f \]

where \( D_e \) is the effective diffusion coefficient of chloride ion transferred within a porous media by diffusive mechanism, which shows relationship with pore structure parameters (Petersen 1958), and \( u \) is the velocity of chloride ion transported by a solution flow. Shackelford and Daniel (1991) and Shackelford and Moore (2013) pointed out that there is a different meaning between \( D_e \) and apparent diffusion coefficient of chloride ion transfer in concrete. Several models have been proposed to estimate \( D_e \) in porous media, where the MQ model (Millington and Quirk 1959) is widely adopted. In the MQ model, \( D_e \) is described by pore structures (i.e., volume fraction, tortuosity factor) and \( D_0 \) [diffusion coefficient of chloride ion in bulk water (m²/s)], which can be expressed as:

\[ D_e = \frac{\theta}{\tau_{MQ}} D_0 \]

where \( \tau_{MQ} = \theta^{0.75} \phi^2 \) is the tortuosity factor and \( \phi \) is the total effective porosity of concrete. It is obvious that the MQ model does not consider the constrictivity factor \( \delta \), which is used to describe the reduction effect of the pore connectivity and electric changes on the walls of the micro-pores during mass transport (Sun et al. 2011; Nakarai et al. 2006). Pore sizes are thought to be the main determinant of constrictivity. Nakarai et al. (2006) de-
fined the constictivity factor $\delta$ as a function of the peak pore radius by Eq. (7), where $p_{\text{peak}}$ is the peak radius of capillary pores (m). The relationship between $\delta$ and $p_{\text{peak}}$ is shown in Fig. 1.

$$\delta = 0.395 \tanh \left[ 4(\lg p_{\text{peak}} + 6.2) \right] + 0.405 \tag{7}$$

The value of constictivity factor $\delta$ is often taken about 0.01 for the fine mature concrete because the small peak radius of capillary pores varying from 20 to 120 nm (Atkinson and Nickerson 1984; Sun et al. 2011). Then, another model to calculate $D_\varepsilon$ proposed by Nakarai et al. (2006) (abbreviated as the NI model) is written in Eq. (8):

$$D_\varepsilon = \theta \cdot \frac{\delta}{e_{\text{NI}}} \cdot D_0 \tag{8}$$

where $\delta$ is the constictivity factor as given in Eq. (7) and $e_{\text{NI}} = -1.5 \tanh (8.0(\phi - 0.25) + 2.5)$ is the tortuosity factor expressing the geometrical property of pore net, which is an intrinsic characteristic describing the actual pathway length of ion transport in the pore spaces. The relationship is shown in Fig. 2.

### 2.2 Unsaturated moisture transport

Free water usually acts as the carrier of chloride ion. Movement of chloride ion within water is called convection, which is described by the velocity $u$:

$$u = K \frac{\partial h}{\partial x} \tag{9}$$

where $K$ is the hydraulic conductivity (m/s) influenced by the saturation of concrete; and $\frac{\partial h}{\partial x}$ is the hydraulic gradient. The Richards equation (Richards 1931) is widely used to characterize the mass transport of water in unsaturated porous media:

$$[C_m + S_n S_m] \frac{\partial H_p}{\partial t} + \nabla \left[ -K(\theta) \cdot \nabla (H_p + D) \right] = 0 \tag{10}$$

where the specific moisture capacity $C_m$ relates variations in fluid volume fraction $\theta$ to the matric head (i.e., $C_m = \partial \theta / \partial \theta$). The storage coefficient $S$ addresses storage changes due to compression and expansion of the pore spaces and the water when the porous medium is fully wet. To model the storage coefficient of concrete, this example uses the specific storage option, which sets $S = \rho g (\chi_f + \theta g)$. Here, $\rho$ is the fluid density (kg/m$^3$), $g$ is the acceleration due to gravity (m/s$^2$), while $\chi_f$ and $\chi_e$ are the compressibility of solid particles (1×10$^{-5}$ m$^2$/kg) and fluid (4.4×10$^{-10}$ m$^2$/kg), respectively. $S_m$ is the effective saturation and $K(\theta)$ is a function that defines how readily the porous media transmits fluid, which increases with fluid content as $K(\theta) = k_e K_e$. Here, $k_e$ denotes the relative hydraulic conductivity and $K_e$ is the hydraulic conductivity (m/s) in saturated concrete. The pressure head $H_p$ (m) is a dependent variable (matric potential driven by hydrostatic pressure and capillary pressure) and $D$ is the coordinate (for example x, y or z) for the vertical elevation (m). The saturated permeability $k_e$ (m$^2$) and the saturated hydraulic conductivity $K_e$ (m/s) are related to the viscosity $\mu$ (Pa·s), density of the fluid $\rho_f$ (kg/m$^3$), and the acceleration of gravity $g$ (m/s$^2$) by $K_e / \rho_f g = k_e / \mu$.

Nonlinearities appear in the Richards equation because $C_m$, $S_n$, and $k_e$ change with $H_p$ and $\theta$. van Genuchten (1980) adopted the Mualem model (Mualem 1976) to propose a simple water retention curve to describe the relationship in $C_m$, $S_n$, $k_e$, $\theta$ and $H_p$ in unsaturated porous media.

$$\theta = \theta_0 + S_n (\theta_e - \theta_0) \tag{11}$$

$$S_n = \frac{1}{1 + \left( a H_p \right)^\alpha} \quad m = 1 - \frac{1}{n} \tag{12}$$

$$C_m = \frac{a m}{1 - m} (\theta - \theta_0) S_n^{\frac{1}{n}} (1 - S_n^{\frac{1}{n}}) \tag{13}$$
2.3 Fluid-solid coupling

Chloride ion penetration into concrete is a multiphysics coupling problem among three physical fields: Fluid-Solid-Solute as indicated in Fig. 3.

Classical fluid mechanics generally assume that the porous media (such as rocks, soils, etc.) are completely rigid, i.e., there is no elastic or plastic deformation in solid skeleton during the seepage process. However, when liquid flows through concrete under hydrostatic pressure, the coupling process between the hydraulic process and mechanical process is bidirectional and is mainly reflected in two aspects: (1) fluid to solid coupling meaning that the change of pore volume of concrete; and (2) solid to fluid coupling meaning that the change of pore volume will cause the change of concrete hydraulic conductivity. Several assumptions are made to discuss the fluid-solid coupling model for unsaturated concrete effectively: (1) water is incompressible; (2) no hysteresis in solid-water characteristic curves; and (3) the air diffusivity. Several assumptions are made to discuss the fluid-solid coupling model for unsaturated concrete effectively: (1) water is incompressible; (2) no hysteresis in solid-water characteristic curves; and (3) the air diffusivity.

Based on the linear elasticity theory, the constitutive relations for the stress and strain under pore water pressure, \( p \), can be described as the following equation (Neuzil 2003; Detournay and Cheng 1993; Zhou et al. 1998).

\[
\begin{align*}
\sigma_{ij} &= \frac{1}{2G} \varepsilon_{ij} - \left( \frac{1}{6G} - \frac{1}{9K'} \right) \sigma_{ii} \delta_{ij} + \frac{1}{3K'} \alpha_p p \delta_{ij} \\
\varepsilon_{ij} &= \frac{1}{2G} \sigma_{ij} - \left( \frac{1}{6G} - \frac{1}{9K'} \right) \sigma_{ii} \delta_{ij} + \frac{1}{3K'} \alpha_p p \delta_{ij}
\end{align*}
\]  

(15)

For the mechanical problem, Eq. (15) can be solved by solving Eq. (15) as follows:

\[
\begin{align*}
\sigma_{ij} &= 2G \varepsilon_{ij} + G \frac{\nu}{1-2\nu} \varepsilon_{kij} - \alpha_p p \delta_{ij} \\
\varepsilon_{ij} &= \frac{1}{2G} \sigma_{ij} + G \frac{\nu}{1-2\nu} \varepsilon_{kij} - \alpha_p p \delta_{ij}
\end{align*}
\]  

(16)

where \( \varepsilon_{ij} \) is the total strain tensor and \( \varepsilon_{ij} = \varepsilon_{aij} + \varepsilon_{pij} + \varepsilon_{pij} \) is the volume strain which is related to effective stress rather than to the total stress (Neuzil 2003; Zhang et al. 2008), \( p \) is the pore pressure (Pa); \( G = E/(2(1+\nu)) \) is the shear modulus (Pa); \( E \) is the Young’s modulus; \( \nu \) is the Poisson’s ratio and \( \delta_{ij} \) is the Kronecker delta defined as 1 for \( i = j \) and 0 for \( i \neq j \). \( \alpha_p = 1 - K/K_s \) is the Biot’s effective stress parameter which depends on the compressibility of the concrete; \( K = 2G(1+\nu)/(3(1-2\nu)) \) is bulk modulus of the porous medium and \( K_s \) is the bulk modulus of the solid grains.

Combined with static equilibrium equation (i.e., \( \delta_{ij} = -F_i \)) and strain-displacement equation (i.e., \( \varepsilon_{ij} = (u_{ij} + u_{ji})/2 \)), the stress control equation for concrete mass deformation in terms of the displacement \( u_i \) and pore pressures \( p \) is as follows:

\[
Gh_{ij} + \frac{G}{1-2\nu} u_{j,ii} - \alpha_p p_{ij} + F_i = 0
\]  

(17)

For saturated concrete, since volume \( V_s \) of the concrete grains and volume \( V_e \) of voids (Zhou et al. 1998), Eq. (18) is obtained:

\[
\begin{align*}
\frac{1}{V} \frac{\partial V}{\partial t} &= \frac{1}{V} \frac{\partial V}{\partial t} + \frac{1}{V} \frac{\partial V}{\partial t} = \frac{\partial \varepsilon_{ij}}{\partial t} \\
\frac{1}{V} \frac{\partial V}{\partial t} &= -\frac{1-\phi}{K_s} \frac{\partial p}{\partial t} + \frac{1}{3K_s} \frac{\partial \varepsilon_{ij}}{\partial t} \\
\frac{1}{V} \frac{\partial V}{\partial t} &= -\nabla q_j - \phi \frac{\partial p}{\partial t} - \frac{\partial \varepsilon_{ij}}{\partial t}
\end{align*}
\]  

(18)

where the change of concrete grains volume \( V_s \) and concrete voids volume \( V_e \) can be described by Eqs. (19) and (20), respectively,

\[
\begin{align*}
\frac{1}{V} \frac{\partial V}{\partial t} &= -\phi \frac{\partial p}{\partial t} - \frac{\partial \varepsilon_{ij}}{\partial t} \\
\frac{1}{V} \frac{\partial V}{\partial t} &= -\nabla q_j - \phi \frac{\partial p}{\partial t} - \frac{\partial \varepsilon_{ij}}{\partial t}
\end{align*}
\]  

(19)

(20)

where \( \varepsilon_{ij} (\varepsilon_{ij} = \varepsilon_{aij} + \varepsilon_{pij} + \varepsilon_{pij}) \) is the volume strain; \( t \) is the time (s); \( q_j \) denotes the water flux/unit area (m/s) and \( \beta_i \) is bulk modulus of pore water (Pa). In Eq. (19), the two terms on the right represent the volume change caused by water pressure and the effective stress, respectively. In Eq. (20), the two terms on the right represent the net volume of water and the water volume changes caused by water pressure, respectively. Substitution of Eqs. (19)
and (20) into Eq. (18) results in Eq. (21).

$$\nabla q_i = -\frac{\partial \xi_i}{\partial t} - \left( 1 - \frac{\phi}{\beta} \right) \frac{\partial p}{\partial t} + \frac{1}{k_{s}} \frac{\partial \sigma_{i}}{\partial t}$$

(21)

Based on thermodynamics of irreversible processes, the water flux is given by \(q_i = -k_{i} \cdot \frac{\partial p}{\partial t} \) in unsaturated concrete, where \(k_{i}\) is the saturated permeability of concrete \((m^2)\). \(\mu\) is the viscosity of water \((Pa \cdot s)\) and \(k_{i}/\mu\) is the permeability tensor \([m^2( Pa \cdot s)^{-1}]\). Then the seepage equation under the effect of fluid-solid coupling can be obtained (Zhou et al. 1998).

$$k_{i} \cdot \frac{k}{\mu} \cdot \nabla^2 p = \alpha \cdot \frac{\partial \mu_{ij}}{\partial t} + \left( 1 - \frac{\phi}{\beta} \right) \frac{\partial p}{\partial t}$$

(22)

It is necessary to know the relationship of parameters to solve the control equations of fluid-solid coupling; that is, Eqs. (17) and (22). According to Zimmerman et al. (1986), Cui and Bustin (2005) and Detournay and Cheng (1993), the relationship between porosity and pore pressure is given by the following equation.

$$\phi = \phi_{0} - (\alpha_{p} - \phi_{b}) \exp \left[ -\frac{1}{K_{s}} \left( (\sigma - \sigma_{0}) + (p - p_{0}) \right) \right]$$

(23)

The relationship that saturated permeability \(k_{s}\) varies with porosity \(\phi\) under the effect of pore pressure \(p\) is considered as a relation \(k_{s} \sim \phi^{\alpha}\) (Cui and Bustin 2005; Detournay and Cheng 1993; Zhang et al. 2008).

In total, the governing partial differential equation of the chloride transfer can be combined as follows:

$$\frac{\partial C}{\partial t} + C \cdot \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left( D_{e} \cdot \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial x} \left( k_{s} \cdot \frac{\partial h}{\partial x} \right) \cdot C$$

(24)

### 3. Numerical Model and Materials

The objective of this study is to validate the feasibility of the whole theory and analyze the sensitivity of some variable parameters. The numerical simulation was carried out by solving partial differential equations. When a 3D concrete model of 0.3 m thick is built, the chloride ion concentration inner concrete is supposed to be zero initially. The initial saturation of concrete is 0.8 and the external water pressure is 1.5 MPa, as illustrated in Fig. 4.

![Fig. 4 Simulation model of tunnel concrete under water pressure.](image)

The standard seawater according to the International Association for the Physical Sciences of the Ocean (IAPSO SSW) and for Chinese Primary Standard Seawater (CP SSW), the chloride ion concentration in the seawater is set at 19000 ppm (i.e., 546 mol/m^3). The density of water is taken as 1000 kg/m^3 and the diffusion coefficient of chloride ion in water, \(D_{c}\), is taken as 1.484 × 10^{-5} m^2/s (Pang et al. 2015). For concrete, the water-cement ratio is selected to 0.5 as a reference and the values of the bulk modulus and shear modulus are 17.5 GPa and 13 GPa, respectively. Referring to the related literature, Table 1 lists other input parameters for the calculation as control.

When solving the governing partial differential equation of the chloride transfer [Eq. (24)], it is essential to gain the definition of effective diffusion coefficient of chloride ion, \(D_{e}\). While in the form of \(D_{c}\), there is some discrepancy between the two models (i.e., the MQ model and the NI model) from different references. Thus, this paper compares the two models to assess their applicability. In the sensitivity analysis, this research mainly discusses the influence of saturated permeability \(k_{s}\), the van Genuchten parameters \((\alpha \text{ and } m)\) (abbreviated as the vG parameters), and binding capacity parameters \((\alpha \text{ and } \beta)\) on the sensitivity of chloride ion transfer. The different moisture characteristic curves (vG-1, vG-2 and vG-3) referred from different literature and a new moisture characteristic curve (i.e., vG-
4), which has the same value of $\alpha$ as for vG-1 and the same $m$ as for vG-2, is defined to make comparative analysis as shown in Fig. 5. In addition, the different chloride ion binding relationships (abbreviated as CBR) are shown in Fig. 6. The existing chloride ion binding relationships based on Eq. (2) (i.e., CBR-1, CBR-2 and CBR-3) and a new chloride ion binding relationship CBR-4 with the same value of $\alpha$ as for CBR-1 and same $\beta$ as for CBR-2, are used to study the sensitivity of the binding capacity parameters.

4. Results and discussion

4.1 Predictive analysis

(1) Influence of fluid-solid coupling

The transient predictive analysis of 50 years with 10-year interval was performed, and the simulation results (pore water pressure, saturation, porosity and permeability) are shown in Fig. 7. Under considering the fluid-solid coupling, it is recognizable that with increase in saturation, the matric pressure decreases, i.e., the pore water pressure increases, which results in the porosity increasing by about 1.17% and the saturated permeability increasing by about 3.3%, meaning that in the areas where saturation changes, the transport of chloride ion will become faster.

![Fig. 5 Moisture characteristic curves for different sets of vG parameters (w/c = 0.5).](image)

![Fig. 6 Chloride ion binding relationship for different binding capacity parameters (w/c = 0.5).](image)

![Fig. 7 Distributions of permeability, porosity, saturation and pore water pressure.](image)

(2) Verification of the multi-mechanism penetration model

To verify the proposed multi-mechanism penetration model, two different time spans of chloride diffusion are discussed for the short-term (150 days) and the long-term (30 years).

For the short-term verification, Long et al. (2008) measured the amount of chloride ions in concrete immersed in sodium chloride solution for 150 days. The test samples were made of a mixture of ordinary Portland cement, ground granular blast furnace slag, river sand and crushed limestone. Tap water was used for mixing the concrete. The water to binder ratio of the concrete was 0.6. The mixing proportions of the test samples were given in Table 2. All samples were immersed into 3.5% NaCl solution after being cured at a temperature of 20°C and 95% relative humidity for 28 days. The experimental results (black point) and fitted curve (red dash line) inferred from Long et al. (2008), the numerical results calculated by MQ model (purple dot dash line), the numerical results calculated by modified MQ model (blue line) and analytical prediction

Table 2 Mix proportions of the test samples in kg/m³ [adopted from Long et al. (2008)].

|       | Cement | Water | River sand | Crushed stone |
|-------|--------|-------|------------|--------------|
| 0 year| 340    | 204   | 650        | 1160         |
| 10 year| 340    | 204   | 650        | 1160         |
| 20 year| 340    | 204   | 650        | 1160         |
| 30 year| 340    | 204   | 650        | 1160         |
| 40 year| 340    | 204   | 650        | 1160         |
| 50 year| 340    | 204   | 650        | 1160         |
results by Fick’s 2nd law (black dot line) are given in Fig. 8. Although Fick’s 2nd law is commonly used to describe chloride ion diffusion into concrete, from Fig. 8, it can be identified that the analytical results by using Fick’s 2nd law just describes the chloride ion diffusion into concrete. Therefore, it shows a good agreement with the experimental data in the diffusion zone (in the case of this analysis, the area with a depth of more than 13 mm). However, in the zone less than 13 mm deep, as the transfer of chloride ions are controlled by convection and diffusion, it has significant differences between analytical results and experimental results.

On the other hand, for the widely adopted MQ model, as it does not consider the effect of constrictivity factors of the concrete, its results are much higher than the analytical and experimental results. Accordingly, in this study, the constrictivity factor was considered into the MQ model. It can be recognized that both in the diffusion zone and in the convection zone, the numerical results by using the revised MQ model given in this paper have a good agreement with the experimental results, meaning that the modified model has the superiority for simulating the transfer process of chloride ion into concrete.

While for the long-term verification, it is discussed whether the diffusion coefficient is within a reasonable range. The effective diffusion coefficient $D_a$ is determined in steady-state diffusion tests, i.e., with a constant chloride flux. The apparent diffusion coefficient $D_p$ obtained in the non-steady-state chloride diffusion and migration tests represent the diffusion of chloride ions in the pore solution of concrete in lab experiments, considering the reaction between the chloride ions and the porous medium (so-called chloride ion binding). As it is hard to obtain the effective diffusion coefficient through long time experiments or actual measurements, the apparent diffusion coefficient obtained from the rapid chloride migration test is used to verify the simulation. Spiesz and Brouwers (2013) through the rapid chloride migration test got the relationship between apparent diffusion coefficient $D_a$ and effective diffusion coefficient $D_p$, as $D_a = D_p \times 0.133$. However, the calculated $D_a$ from rapid chloride migration test is about 30% larger than that obtained from the non-steady-state diffusion test. Therefore, $D_a$ must be revised to get the steady-state apparent diffusion coefficient $D_{ap}$, as $D_{ap} = 1.3 \times D_p$. By reviewing a large amount of literatures and experiments, Song et al. (2009) concluded that the $D_{ap}$ obtained from experiments mostly ranges from $2.0 \times 10^{-12}$ to $5.5 \times 10^{-12}$ m²/s. As shown in Fig. 9, the apparent diffusion coefficient and revised apparent diffusion coefficient at 30 years by the two numerical models in this paper were calculated. It can be identified that revised $D_{ap}$ of the MQ model and the NI model ranges from $2.4 \times 10^{-12}$ to $5.25 \times 10^{-12}$ m²/s and $2.25 \times 10^{-12}$ to $3 \times 10^{-12}$ m²/s respectively, which has a good agreement with the experiment results. The agreement means that the model used in this study reveals the real situation of chloride ion transfer and the multi-mechanism penetration model is computable.

(3) Chloride ion profile and modified analysis to the MQ model
In this part, from the results of comparison of concentration profiles as shown in Fig. 10. It can be identified that the concentration of chloride ion in the same period calculated by using the MQ model is significantly larger than that by using the NI model, which implies that constrictivity factor, $\delta$ may have an immense impact on the migration of chloride ion. Therefore, based on the theory of the NI model, the factor of constrictivity with the value of 0.01 is considered to modify the MQ model. Afterwards, the calculation results of the NI model and the modified MQ model have a good agreement; thus, the modified MQ model is concluded to be reliable and acceptable.

4.2 Sensitivity analysis
The sensitivity of input parameters is analyzed in terms of the resulting chloride profiles at 30 years. Several
interesting observations can be obtained by examining the effects of different parameters on the sensitivity of the predicted chloride ion profiles. It should be noted that the parameters are taken from many literatures to describe concrete with w/c = 0.5. In addition, there are also some sets of parameters created by the combination of existing data to make more detail discussion.

(1) Sensitivity to saturated permeability $k_s$

A comparison of chloride ion concentration profiles resulting from different values of saturated permeability $k_s$ (i.e., $3 \times 10^{-22}$ m$^2$, $3 \times 10^{-21}$ m$^2$ and $3 \times 10^{-20}$ m$^2$) after 30 years is presented in Fig. 11. The diffusion process and convection process are presented separately to obtain the sensitivity in detail. The result shows that with increase in saturated permeability, the convection depth increases obviously, while the influence on diffusion is negligible. It is found that the convection depths are around 10 mm, 33 mm, and 100 mm under the effect of saturated permeability of $3 \times 10^{-22}$ m$^2$, $3 \times 10^{-21}$ m$^2$ and $3 \times 10^{-20}$ m$^2$, respectively, which means that with the increase in saturated permeability, the convection zone depth increases by a factor of 2.

(2) Sensitivity to vG parameter and initial saturation $S_{m0}$

It is more sensitive for the initial saturation $S_{m0}$ than the vG parameters ($a$ and $m$) in affecting the chloride ion transfer, as shown in Fig. 12. It is probably because the saturation affects not only diffusion by effective diffusion coefficient, $D_e$ but also convection by permeability, $k_s$. When investigating carefully at the distribution curve of $S_{m0} = 0.8$, it is recognizable that the difference of the gap between vG-1 to vG-4 is considerably larger than that between vG-2 to vG-4. It is identifiable that vG-1 and vG-4 share the same value of $a$, while vG-2 and vG-4 share the same value of $m$, it is not difficult to conclude that $m$ is a dominant factor in vG parameters.

(3) Sensitivity to chloride binding isotherm $k_p$

The Freundlich isotherm is adopted to describe the binding capacity. It is found that when the free chloride ion concentration is extremely small, the calculation will not converge, so here 50 mol/m$^3$ is set as the threshold concentration, and if the concentration is lower than the threshold value, $k_p$ will be taken as a very small constant. As shown in Fig. 13, in the saturated zone the bound chloride ion content and binding isotherm are constant. As the depth increases, the free chloride ion concentration decreases, which results in decrease in bound chloride ion but increase in $k_p$.

As mentioned in Fig. 6, CBR-4 takes only different
value of $\beta$ to CBR-1, and CBR-4 takes the only different value of $\alpha$ to CBR-2. Figure 14 shows the predicted chloride ion distribution calculated by different binding parameters ($\alpha$ and $\beta$). It can be found from the profile that the diffusion process is affected by the change in binding parameters, but the influence is not extremely significant in total. The distribution curve calculated by the binding parameters of CBR-4 is closer to CBR-2 than to CBR-1. Then it can be carefully concluded that $\beta$ may be a dominant factor in the binding parameters.

5. Conclusions

The model of chloride ion penetration into unsaturated concrete under external water pressure is further extended by considering not only the relationship of multiple mechanisms but also the influence of fluid-solid coupling. The numerical simulation approach is formulated to describe the transfer process. Then several sets of input parameters are discussed to study the sensitivity to the model. The following conclusions can be drawn:

1. As proposed in this work, the transfer model may be very versatile in the microscopic perspective. It can be found that the porosity, saturated permeability and matric pressure of concrete increase with increase in saturation when considering the fluid-solid coupling. In this paper, the porosity increased by about 1.17% and the saturated permeability increased by about 3.3%, which results in increase in chloride ion transfer speed.

2. When analyzing the expression of the effective diffusion coefficient, the MQ model was widely adopted in the past literatures while the NI model was proposed in another form. As the MQ model did not consider the reduction effect of the pore connectivity and electric changes on the walls of the micro-pores, the MQ model should be modified. After comparing the predicted profile with the modified MQ model and NI model, the results can be concluded that the modified MQ model with considering constricitivity factor shows a good agreement with the NI model. In addition, the apparent diffusion coefficient of both models has a good agreement with the experiment results. Therefore, the model in this paper is able to simulate the real situation of chloride ion transfer and the multi-mechanism penetration theory is feasible.

3. The results of sensitivity analysis performed with different input parameters show that changes of all the parameters have effects on the predicted result, so it is essential to choose appropriate values of parameters to obtain a reasonable estimate of simulation. From the sensitivity study of different sets of parameters, it can be concluded that the key sensitivity factor are the parameters related to moisture transport (e.g., saturated permeability, initial saturation, and the vG parameter $m$) while the factor of chloride binding isotherm shows less sensitivity.

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