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MODELING OF CHLORIDE TRANSPORT IN CONCRETE STRUCTURES

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ABSTRACT :

Chloride-induced corrosion of steel bar is one of the severe problems for long term durability of reinforced concrete structures. Modeling chloride diffusion in concrete structures is very useful for structural engineers and/or management agency for predicting the service life and scheduling the maintenance and/or rehabilitation plan of reinforced concrete structures. In this paper, a theoretical and computational model for chloride penetration into concrete structures is presented. The governing equations are accounted for the transport mechanism of chloride ions, moisture, and temperature. This is related to concrete structures which are always found in non-saturated and non-isothermal conditions. The coupled effects among chloride, moisture, and temperature are considered and included in the model. The coupling parameters are evaluated based on the available test data and incorporated in the governing equations. Then, the coupled partial differential equations are solved by the finite element method.

KEYWORDS : Modeling, Chloride, Concrete, Coupling effect

1. Introduction

Some reinforced concrete structures such as bridge decks, parking areas, and marine structures in splash and tidal zones are frequently exposed to chloride-rich environments from deicing salts or sea water. This condition leads to the long-term durability problem due to chloride-induced corrosion of reinforcement of such structures. As a result, it eventually causes spalling, cracking, and delamination of concrete cover thus reducing load bearing capacity and aesthetic feature of structures. In order to manage the maintenance and/or rehabilitation plan, we need to develop the mathematical model to predict chloride penetration into concrete. This can be performed using the simplified model based on Fick's law which is presented in this paper.

In saturated and isothermal conditions, chloride ions diffuse in concrete mainly due to concentration gradient. This means that there are no moisture and temperature effects on chloride penetration mechanism. On the other hand, in non-saturated condition, there is a coupled effect between chloride and moisture transport in concrete that the diffusion rate of chloride ions is accelerated by moisture gradient similar to moisture which is influenced by chloride diffusion process [1-2]. For non-isothermal condition, by increasing temperature, it can increase the rate of chloride ingress into concrete [3]. It is evident from the study by Khoshbakht et al. [4] that moisture transport in masonry walls is affected by heat flow. As the actual condition of reinforced concrete exposed to chloride ions is most likely in non-saturated and non-isothermal conditions, therefore, in this paper, the simplified mathematical model of chloride diffusion in concrete is presented and derived based on the Fick's law. The governing equations are taken into account the coupled effects among chloride, moisture, and temperature. The numerical solutions are solved by using finite element method.

2. Basic Formulation of Governing Equations

The flux of chloride ions transport in porous media (i.e. concrete) based on the Fick's law can be described as follow:

$$J_{Cl} = -D_{Cl}\nabla C_f \tag{1}$$

where 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 moisture content in concrete can be expressed by water content (w) or by pore relative humidity (H). In this study, pore relative humidity is used to represent the moisture content in concrete. Pore relative humidity is considered as a combined indicator of liquid water and water vapor [5]. The moisture flux (J_H) can be described in terms of the gradient of pore relative humidity as follows:

$$J_H = -D_H\nabla H \tag{2}$$

in which D_H is the humidity diffusion coefficient and H is the pore relative humidity.

For the heat flow in concrete materials, the heat flux can be simply expressed as the well-known Fourier's law of heat conduction equation:

$$J_Q = -D_T\nabla T \tag{3}$$

in which J_Q is the heat flux, $D_{T\text{-}T}$ is the thermal diffusivity of concrete, and T is temperature.

As described previously, the governing equations among chloride, moisture, and temperature are fully coupled and then these coupled diffusion equations must be solved simultaneously. Therefore, the flux of chloride ions (J_{Cl}) in non-saturated and non-isothermal concrete can be written as:

$$J_{Cl} = -\left(D_{Cl}\nabla C_f + D_{Cl-H}\nabla H + D_{Cl-T}\nabla T\right) \tag{4}$$

Where $D_{Cl\text{-}H}$ and $D_{Cl\text{-}T}$ are the coupling parameters due to the effect of moisture and temperature on chloride diffusion (Soret effect), respectively. Similar to chloride flux, Moisture and heat flux, Eqs. (2) and (3), can be modified by adding the coupling terms, which are taken into account the influence of chloride and temperature diffusion on moisture flux (Soret effect), and the effects of chloride and moisture transport on heat flow (Dufour effect) expressed as Eq. (5) and (6), respectively:

$$J_H = -\left(D_{H-Cl}\nabla C_f + D_H\nabla H + D_{H-T}\nabla T\right) \tag{5}$$

$$J_Q = -\left(D_{T-Cl}\nabla C_f + D_{T-H}\nabla H + D_T\nabla T\right) \tag{6}$$

The mass balance equations of chloride, moisture, and heat transport in concrete can be described as Eqs. (7), (8), and (9), respectively:

$$\frac{\partial C_t}{\partial t} = \frac{\partial C_t}{\partial C_f}\frac{\partial C_f}{\partial t} = -\nabla J_{Cl} = \nabla\left(D_{Cl}\nabla C_f + D_{Cl-H}\nabla H + D_{Cl-T}\nabla T\right) \tag{7}$$

$$\frac{\partial w}{\partial t} = \frac{\partial w}{\partial H}\frac{\partial H}{\partial t} = -\nabla J_H = \nabla\left(D_{H-Cl}\nabla C_f + D_H\nabla H + D_{H-T}\nabla T\right) \tag{8}$$

$$\frac{\partial Q}{\partial t} = \frac{\partial Q}{\partial T}\frac{\partial T}{\partial t} = -\nabla J_Q = \nabla\left(D_{T-Cl}\nabla C_f + D_{T-H}\nabla H + D_T\nabla T\right) \tag{9}$$

where $\partial C_t/\partial C_f$, $\partial w/\partial H$, and $\partial Q/\partial t$ are the chloride binding capacity, moisture capacity, and heat capacity. The coupling terms among chloride, moisture, and temperature will be discussed later.

3. Material Model

There are ten material parameters including in the governing equations, Eqs. (7), (8), and (9). The determination of these material parameters will be discussed in this section.

3.1 Chloride Binding Capacity ($\partial C_t/\partial C_f$)

By using the model recently developed by Xi and Bazant [6], chloride binding capacity can be expressed as:

$$\frac{dC_f}{dC_t} = \frac{1}{1 + \dfrac{A10^B\beta_{C-S-H}}{35{,}450\beta_{sol}}\left(\dfrac{C_f}{35.45\beta_{sol}}\right)^{A-1}} \tag{10}$$

where A and B are two material constants related to chloride adsorption and equal to 0.3788 and 1.14, respectively [7]. The binding capacity depends on the two parameters, β_{sol} and β_{C-S-H}. More information on these two parameters can be found in Xi and Bazant [6].

3.2 Chloride Diffusion Coefficient (D_{Cl})

The chloride diffusion coefficient, D_{Cl}, can be obtained from a model developed by Xi and Bazant [6]:

$$D_{Cl} = \left\{\left[\frac{1}{4} + \frac{28-t_0}{300}\right](w/c)^{6.55} + \frac{(28-t_0)}{62{,}500}\right\}\frac{2\left[1-\left(V_p - V_p^c\right)\right]}{S^2}\left(V_p - V_p^c\right)^f\left[1 - k_{ion}\left(C_f\right)^m\right] \tag{11}$$

where t_0 = curing time; w/c = water-to-cement ratio; m = 0.5; $k_{ion} = \sqrt{70}$; f = 4.2; $V_p^{\,c}$ = 3%; S = internal surface area of cement paste which can be estimated by the monolayer capacity V_m of adsorption isotherm of cement paste since V_m is proportional to S [8]; V_p = porosity of cement paste and can be approximately estimated by using the adsorption isotherm at saturation. Eq. (11) shows the general effects of various parameters on the diffusion coefficient. For example, when w/c increases, the diffusion coefficient increases; with a longer curing time, the diffusion process is slower; and when the concentration of free chloride is higher the diffusion coefficient is lower (called concentration effect).

3.3 Moisture Capacity (∂w/∂H)

The moisture capacity of concrete can be determined by taking the average of the moisture capacities of cement paste and aggregate as proposed by Xi et al. [9]

$$\frac{dw}{dH} = f_{agg}\left(\frac{dw}{dH}\right)_{agg} + f_{cp}\left(\frac{dw}{dH}\right)_{cp} \tag{12}$$

in which f_{agg} and f_{cp} are the weight percentages of the aggregate and cement paste, respectively; $\left(\frac{dw}{dH}\right)_{agg}$ and $\left(\frac{dw}{dH}\right)_{cp}$ are the moisture capacities of aggregate and cement paste, respectively, which can be calculated based on the model proposed by Xi et al. [8, 10] and Xi [11-12].

3.4 Humidity Diffusivity (D_H)

The moisture diffusivity of concrete can be predicted by the composite model developed by Christensen [13]:

$$D_H = D_{Hcp}\left(1+\frac{g_i}{[1-g_i]/3+1/[(D_{Hagg}/D_{Hcp})-1]}\right) \tag{13}$$

in which, g_i is the aggregate volume fraction, D_{Hcp} is the humidity diffusivity of the cement paste and D_{Hagg} is the humidity diffusivity of the aggregates. The humidity diffusivity of aggregates in concrete is very small comparing with the diffusivity parameters of concrete and can be neglected in Eq. (13). The humidity diffusivity of cement paste can be predicted by the empirical model developed by Xi et al. [10].

3.5 Coupling Parameters (D_{Cl-H}, D_{H-Cl}, D_{Cl-T}, D_{H-T}, D_{T-Cl}, D_{T-H})

According to Ababneh and Xi [2] and Abarr [1] studies, both coupling parameters, D_{H-Cl} and D_{Cl-H}, are chloride concentration dependent and they can be expressed in terms of free chloride concentration as follows:

$$D_{Cl-H} = \varepsilon Cl_f \tag{14}$$

$$D_{H-Cl} = \delta Cl_f \tag{15}$$

in which ε and δ are two constants obtained by curve fitting which are 0.19 and 0.52, respectively [14]. The coupling parameter due to the effect of temperature on chloride diffusion, D_{Cl-T}, can be evaluated based on the experimental study by Isteita [3] described as Eq. (16).

$$D_{Cl-T} = aC_f f_1(t) f_2(T) \tag{16}$$

where a is the constant which can be estimated by curve fitting at different ages of concrete, different concrete mix design parameters, and temperature conditions on exposed surface. The proposed value of a equals to $5x10^{-8}$. The first factor, $f_1(t)$, is the factor accounted for the effect of the aging of concrete which is relevant to hydration reactions of cement paste given by Eq. (17):

$$f_1(t) = 4 * t^{-1} \tag{17}$$

in which t is the aging 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:

$$f_2(T) = Exp(0.1*\frac{U}{R}(\frac{1}{T_{ref}}-\frac{1}{T})) \tag{18}$$

where U is the activation energy of the diffusion process; R is the gas constant; and T and T_{ref} are current and reference temperatures, respectively. Based on the Soret effect, the heat flow in concrete can accelerate diffusion rate of not only chloride ions but also moisture. The parameter D_{H-T} can be determined by the model proposed by Khoshbakht et al. [4] expressed as:

$$D_{H-T} = \rho_0 \begin{pmatrix} 1.67x10^{-8}\theta^5 - 3.99x10^{-6}\theta^4 \\ +2.58x10^{-4}\theta^3 - 4.14x10^{-3}\theta^2 \\ +0.216\theta - 0.035 \end{pmatrix} x10^{-3} \tag{19}$$

$$\theta = 226.68H^3 - 247.75H^2 + 123.45H + 0.1076 \tag{20}$$

in which ρ_0 = 2,200 (kg/m^3), θ is the moisture content, and H is relative humidity. The effect of latent heat diffusion can be negligible [4] so that the parameters D_{T-H} and D_{T-Cl} are not included in the governing equations.

4. Numerical Analysis

A concrete sample, as shown in Fig. 1, is numerically analyzed using finite element method. 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 outside and inside the concrete sample is 100% RH and 50% RH, respectively. The initial temperature outside and inside specimens is specified as 35 °C and 20 °C. This means there are moisture and temperature gradients moving from outside to inside specimen. From this point of view, chloride concentration gradient is contributed by not only concentration gradient itself but also moisture and temperature gradients. The concrete sample is divided into 400 elements and 451 nodes using isoparametric elements for finite element analysis. The defined material parameters and input data for the numerical analysis related to the governing equations are shown in Table 1.

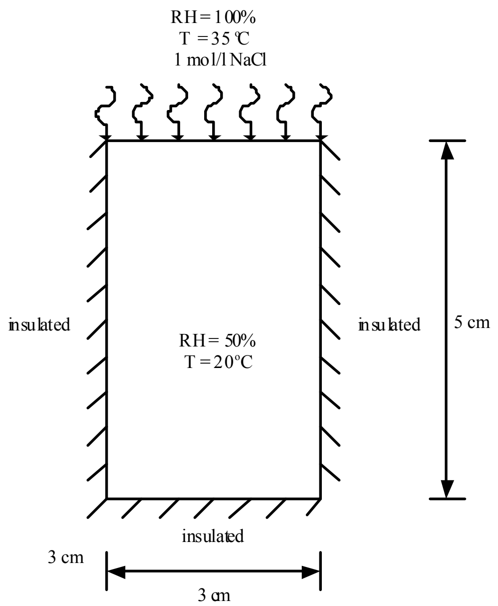

Fig. 1 Concrete sample used in the numerical analysis

5. Numerical Results and Discussion

Fig. 2 shows the trends of free chloride concentration at different times of exposure at non-saturated condition and temperature variation considered. It is evident from Fig. 2 that the concentration of free chloride decreases with increasing depth from the top surface. The initial chloride concentration inside concrete sample is assumed to be zero so that chloride ions ingress from outside to inside specimen. The distribution profiles also demonstrate that, at the fixed depth, the free chloride concentration is higher when the exposure time is longer. The effect of moisture and heat transport on chloride concentration profiles at 10, 50, and 100 days of exposure can be seen from Figs. 3, 4, and 5, respectively. As observed from these figures, at the fixed depth, the chloride concentration at non-saturated condition is higher than saturated state. This is because the chloride concentration gradient is influenced by moisture diffusion. This is called "the coupled effect". As a result, the rate of chloride diffusion is dominated not only by concentration itself but also by the coupling effect due to moisture transport. Figs. 3, 4, and 5 also show that when temperature variation is involved, the changes of chloride concentration can be observed. This is due to the coupling effect among chloride, heat, and moisture diffusion that heat flow can accelerate the diffusion rate of both moisture and chloride. Therefore, it can be concluded that the coupled effect of temperature variation and moisture transport on chloride diffusion in concrete is very significant.

Table 1 Material parameters and input data for concrete sample

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

§ The values are taken from Isgor and Razaqpur [15].

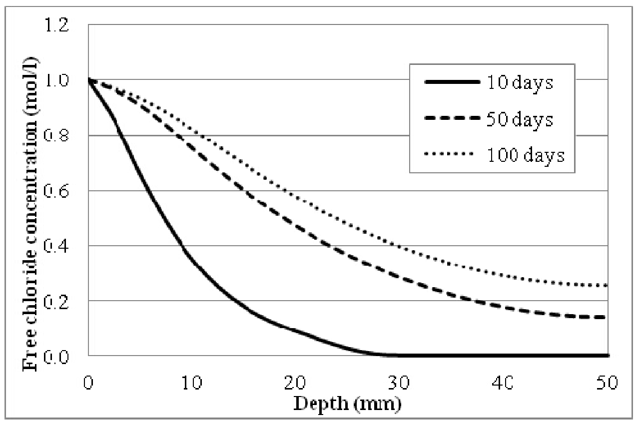

Fig. 2 Free chloride concentration profiles at different times of exposure

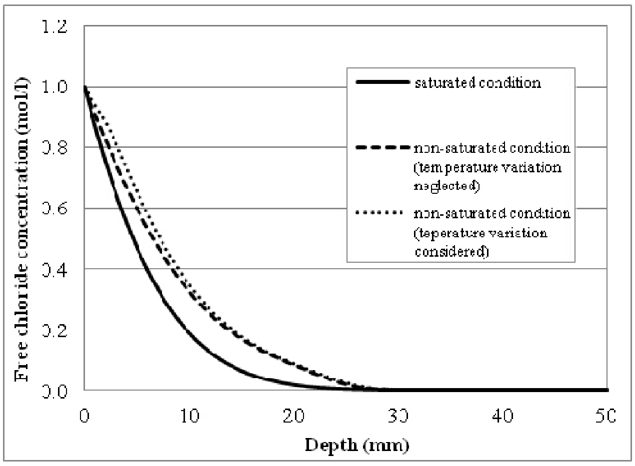

Fig. 3 Free chloride concentration profiles at 10 days of exposure

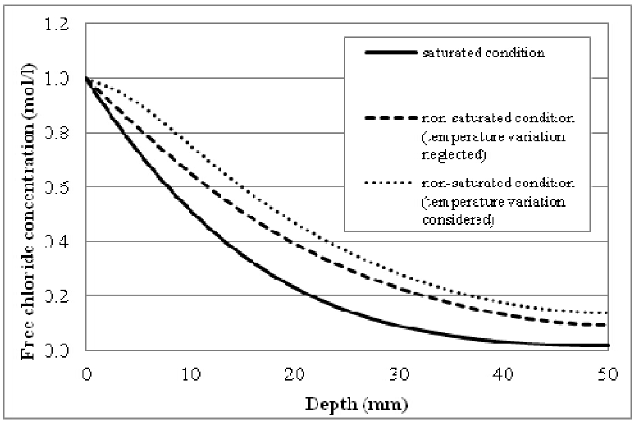

Fig. 4 Free chloride concentration profiles at 50 days of exposure

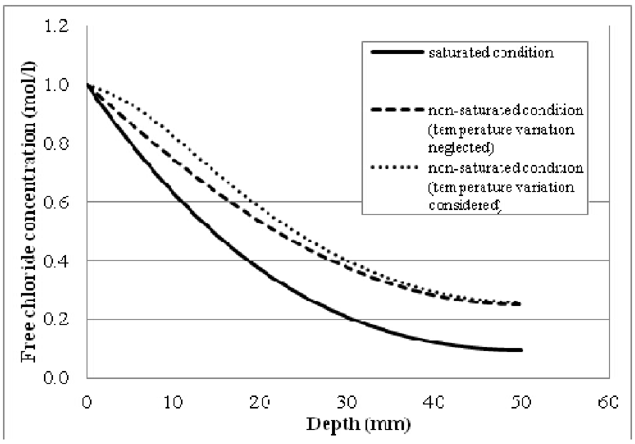

Fig. 5 Free chloride concentration profiles at 100 days of exposure

Figs. 6, 7, and 8 illustrate the influence of temperature variation on moisture profiles at 10, 50, and 100 days of exposure, respectively. It is evident that, at non-saturated condition, when the effect of temperature variation is considered, the moisture is higher. This increasing moisture is due to the influence of heat flow that can increase the chloride concentration by accelerating the rate of carrying chloride ions. Thus, from chloride concentration profiles as shown in Figs. 3, 4, and 5, it can be concluded that the moisture diffusion and heat transfer have remarkable influences on chloride penetration into concrete. When compared to the simple model which employs Fick's second law and includes everything in order to modify the chloride diffusion coefficient, so-called apparent chloride diffusivity, this present prediction model is more comprehensive. The model takes into account not only the coupling parameters but also several parameters which have different physical meanings and can be evaluated in different ways. This is an advantage and improvement of this model that can be used to simulate chloride diffusion in concrete structures close to the reality which is frequently found in non-saturated and non-isothermal conditions.

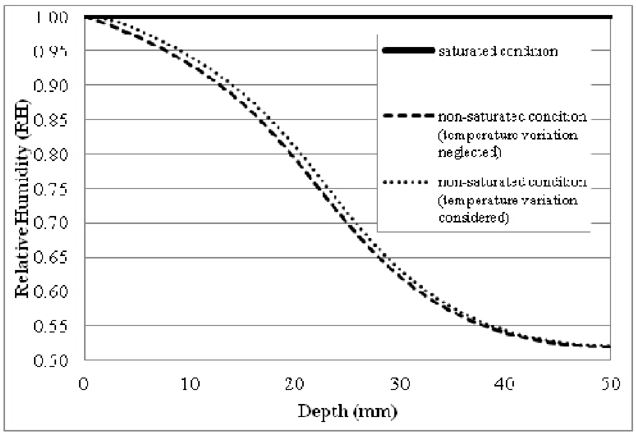

Fig. 6 Moisture profiles at 10 days of exposure

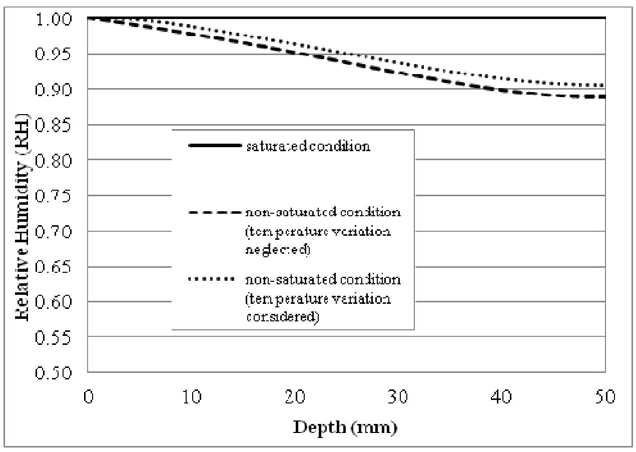

Fig. 7 Moisture profiles at 50 days of exposure

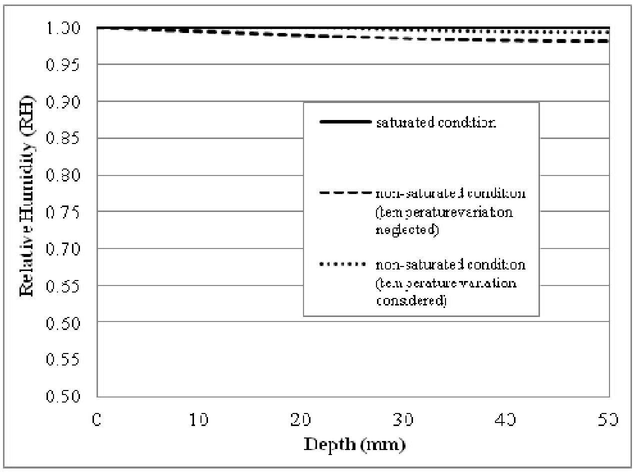

Fig. 8 Moisture profiles at 100 days of exposure

6. Conclusions

(1) A mathematical model is developed based on Fick's law for chloride penetration into concrete. A partial differential equation of chloride diffusion in concrete is modified by taking into account the influences of moisture diffusion and temperature variation. The diffusing equation of moisture is formulated based on Fick's law which is modified by including the effect of temperature variation. Heat flow in concrete is described by Fourier's law.

(2) The governing equations are coupled all together that is the effect of moisture transport and temperature variation on chloride diffusion is considered, as well as the influence of diffusing chloride ions on moisture movement is also taken into account. All coupling effects are expressed explicitly in the governing equations with additional terms representing the coupling mechanisms.

(3) The transport parameters related to chloride and moisture diffusion are characterized by material models. These models are developed for chloride diffusion coefficient, chloride binding capacity, moisture diffusivity, and moisture capacity. Some of these parameters are accounted for concrete mix design factors such as water cement ratio, curing time, and type of cement.

(4) The material models for coupling parameters between chloride and moisture diffusion are developed by using available test data. And, the parameters corresponding to the effect of temperature on chloride and moisture diffusion are obtained from available material models.

(5) Temperature variation has a remarkable influence on moisture and chloride distribution profiles. In non-saturated concrete, chloride gradient is accelerated by moisture movement which it can carry chloride ions. Particularly on non-saturated and non-isothermal (temperature variation considered) conditions, chloride distribution profiles at any times of exposure is strongly influenced not only by the effect of moisture movement but also by heat flow. The present examples show that the coupling effect is very significant.

(6) Compared to the simple model which uses Fick's second law and takes into account everything to determine the apparent chloride diffusivity, this present model has advantages and improvements in the aspect of modifying the diffusing equations of chloride by incorporating the coupling parameters.

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