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CHLORIDE-BINDING ISOTHERMS IN CONCRETE SUBMITTED TO NON-STEADY-STATE DIFFUSION-MIGRATION MODEL

Wen-Hu Tsao¹, Ming-Te Liang², and Ta-Peng Chang³

Key words: concrete, chloride, diffusion, linear binding, Freundlich isotherm, Langmuir isotherm.

ABSTRACT

We propose a mathematical non-steady-state, time/depth dependent diffusion-migration model based on the modified Fick's second law of diffusion. It considers the effects of different chloride binding mechanisms for the transport process of chloride ions diffused in a porous concrete on the variation of its chloride profile. Four different chloride-binding isotherms, i.e., no binding, linear binding, Langmuir binding and Freundlich binding, together with the time/depth dependent chloride diffusivities are investigated. Results of this study show that the variations of amounts of available free chloride ions in the solution of saturated concrete resulting from different chloride-binding isotherms have significant effects on the chloride profile. Comparison between the analytical solution of the proposed mathematical model and previous experimental data shows a satisfactory agreement for the chloride concentrations 0.05 M and 0.1 M. The orders of reduction amount of chloride diffusivities from large to small are found to be in the following sequence: (1) no binding isotherm, (2) Freundlich binding isotherm, (3) Linear binding isotherm, and (4) Langmuir binding isotherm.

I. INTRODUCTION

The chloride diffusion coefficient (or diffusivity) calculated

from the chloride profile (i.e., chloride concentration versus depth) is one of most important parameters related to the concrete durability because this parameter reflects the capability of concrete to resist the transport of chloride ions into a concrete structure. The diffusivity of porous concrete is conventionally determined by the method of either the diffusion cells or the immersion of specimen in a solution. The processes of these methods are extremely slow, often requiring months or years to obtain results, such that they cannot come upon engineering requirements for a rapid estimation on the validity of new materials and treatments of existing deteriorating structures. The application of an electrical field to accelerate the ionic transport becomes a practical approach to reduce the testing time. The chloride ions on concrete surface may enter the interior of porous concrete from various sources through pore structure where the chloride ion either being physically and chemically bound to the cement hydrates (bound chlorides, C_b), or being dissolved in the pore solution (free chlorides, C_f). Only such free chlorides are expected to account for initiating the process of corrosion, because they can continue to penetrate through the concrete cover under this condition (Martín-Pérez et al., 2000).

Numerous researchers have investigated the effect of chloride binding. Sergi et al. (1992) postulated that chloride binding in concrete was owing to physical and chemical absorption. They used the Langmuir adsorption isotherm (Glassstone 1960) to model chloride diffusion. Xi and Bazant (1999) provided the Freundlich isotherm which was a modified relationship between bound and free chlorides. Tang and Nilsson (1993) found that the Freundlich isotherm efforts were more appropriate for high chloride concentrations whereas the Langmuir isotherm efforts were for low chloride concentrations. Sandberg (1999) discovered that the amount of bound chloride increased as the concentration of hydroxide ions in the pore solution decreased. He also found that the relationship between free and total chloride in concrete was nearly linear provided that a linear chloride and hydroxide ion gradient existed. Martín-Pérez et al. (2000) studied the expression in various mathematical models of chloride binding isotherms and discovered that the evalu-

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ated service life was longer with considering the binding effect than that without.

Matano (1993) used Boltzmann's method to solve the modified Fick's second law of diffusion, in which the coefficient of diffusion was treated as a function of concentration (i.e., a function of time and depth), in conjunction with different initial and boundary conditions for analyzing the nickel-copper diffusion system. This approach was called the Boltzmann-Matano methodology. Tumidajski et al. (1995) applied the Boltzmann-Matano methodology to calculate the non-steady state chloride diffusion coefficients for concrete. It was discovered that the chloride diffusion coefficients were depended on time and depth/concentration and were expressed as a linear function of the Boltzmann variable. Tang (1999) showed clearly that the effective chloride diffusion coefficient was not a constant but a complicated function of concentration. The impact of the different chloride binding relations on the time-dependent chloride penetration profiles was studied by Martín-Pérez et al. (2000). They used the finite difference method to solve the chloride mass conservation with the modified Fick's second law of diffusion, where the diffusivity was assumed to be not a constant, for chloride binding in service life predictions of a concrete structure subjected to submerged in seawater and exposed to de-icing salts. Sun et al. (2008) applied the Kirchhoff's transformation together with Laplace's transformation methods to solve a non-steady-state one-dimensional diffusion equation when the diffusion coefficient was represented as a function of time, depth and concentration of chloride for concrete exposed to chloride environment. Sun et al. (2010) used this analytical solution to predict service life of concrete structures exposed to a chloride environment. Based on this model, the results illustrated by the numerical examples were compared with those given by the LightCon model (Maage et al., 1995; Poulsen, 1995; Maage et al., 1996; Poulsen and Mejlbro, 2006). Liang et al. (2011) used the analytical solution obtained by Sun et al. (2008), the experimental data and approximate solution by Martín-Pérez et al. (2000), and four kinds of chloride binding isotherm (i.e., no, linear, Langmuir, and Freundlich binding) to predict the service life of a concrete structure exposed to chloride environments. They found that the percentage errors, the difference between the true value of analytical solution and the approximate value of approximate solution, for the case of Freundlich's binding were higher than those for the cases of both no binding and linear binding when both service life and concrete cover increased. Liang et al. (2012) applied same theoretical model to study the effect of diffusions with induced chloride binding on the life predictions for existing reinforced concrete bridges. They showed that the Langmuir adsorption isotherm was suitable for bridge deck with small concrete cover whereas the linear binding was suitable for pier and abutment with large concrete cover. Sun et al. (2012) used the diffusion-reaction model, which was based on the Fick's second law of diffusion (the diffusion coefficient was assumed to be not constant) to establish a mathematical formulation for an irreversible first-order chemical

reaction, to clearly describe the diffusion mechanism of chloride diffusion process. They indicated that the diffusion-reaction model had predicted a longer service life than that with the total and free chloride diffusion models where the influence of chemical reaction during the chloride diffusion process was not considered. Tang and Nilsson (1992) used the diffusion-migration model, which was based on the Fick's second law of diffusion with the diffusivity being assumed to be constant under an electric field, to rapidly determine the chloride diffusivity of concrete. Based on the Nernst-Planck equation in a cylindrical coordinate and time domain, Liang et al. (2010) applied the diffusion-migration model with the diffusivity being assumed to be constant to evaluate the transport phenomenon of chloride-ions in concrete. By comparing the relationships between the chloride concentration and time with the Nernst-Planck equation, they discovered that the analytical results obtained from solutions based on two-dimensional coordinates and time domain were closer to the experimental results than those from one-dimensional consideration like the case of using the Fick's second law of diffusion with non-constant diffusivity under an electric field. Castellote et al. (1999) experimentally studied the chloride-binding isotherms of concrete subjected to a non-steady-state diffusion-migration process.

As a summary, although previous published studies have shown that the variations of chloride-binding mechanism have significant effects on the chloride diffusion-migration process and chloride profile of porous concrete, up to date, there are still no studies attempted to predict the chloride-binding isotherms in concrete by diffusion-migration model. This may be a shortcoming in that the experimental results of chloride profile obtained from different chloride-binding isotherms in previous studies may have led to an under- or over-estimation of the degree of chloride-binding. As a result, the major purpose of this paper is to use the analytical solutions of a non-steady-state, time/depth dependent diffusion-migration mathematic model to assess the variation of chloride profile of concrete with four different chloride-binding isotherms, i.e., no binding, linear binding, Langmuir binding and Freundlich binding. In order to justify the validity of these four isotherm models, the analytical results are compared with the experimental data obtained by Castellote et al. (1999). The conclusion of the present study may serve as a proper reference for predicting the chloride-binding mechanism in concrete.

II. THEORETICAL FORMULATION

1. Nernst-Planck's Equation

As the chloride flux becomes constant, the general equation that describes transport processes in solution is the Nernst-Planck's equation (Andrade, 1993)

$$J = -D \frac{\partial C}{\partial x} - z \frac{FE}{RT} DC + C_u \quad (1)$$

where J is the constant chloride flux, $C(x,t)$ is the chloride content dependent on depth x and time t , D is the diffusion coefficient of chloride ion, z is the ions valence (for chloride ion, $z = -1$), F is the Faraday constant ($F = 96500$ Coul/mole), R is the gas constant ($R = 8.314$ J/mole · K), T is the Kelvin temperature (K), $E = \Delta V/L$ in electric field, in which ΔV is the potential drop across the tested concrete specimen with length L , and u is the velocity of solute. The first, the second and the third terms of Eq. (1) are the contribution due to diffusion, migration, and convection, respectively. Since the concrete is saturated, the velocity of solution can be neglected. If the concrete is partially saturated or in the environmental dry-wetting conditions, then the velocity of solution should be considered. Under the influence of an electrical field with 12 voltages $< V < 30$ voltages across the concrete sample, the contribution of diffusion in concrete is small and can be neglected, and then, only the migration due to the electrical field need to be considered. If the electrical field with 6 voltages $\leq V \leq 12$ voltages, then both the diffusion and migration contribution should be considered. This is in agreement with the concept of Bourbatache et al. (2012). They pointed out that for a weak-imposed electrical field, or in natural diffusion, the asymptotic expansion of Nernst-Planck equation results in a macroscopic model coupling diffusion and migration at the same order. If the electrical field with 30 voltages $\leq V \leq 60$ voltages, the both the migration contribution and the temperature effect should be taken into account. Castellote et al. (1999) applied the voltage of 12 V for their experimental work and just considered the migration due to the electrical field. Thus, their experimental results will be compared with the predicted results from the proposed model in this study, which has taken into account both the diffusion and migration contribution due to the electrical field with 6 voltages $\leq V \leq 12$ voltages.

2. Non-Stead-State Diffusion-Migration Model

A one-dimensional partial differential equation (PDE) of non-steady-state time/depth dependent diffusion-migration model and its initial and boundary conditions for a porous solid can be written as

$$PDE: \frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(D(x,t) \frac{\partial C(x,t)}{\partial x} \right) - D(x,t)a \frac{\partial C(x,t)}{\partial x}, \quad a = \frac{zFE}{RT} \quad (2a)$$

$$IC: C(x,0) = 0 \quad (2b)$$

$$BC: C(0,t) = C_s \quad (2c)$$

$$C(x \rightarrow L, t_m) = 0 \quad (2d)$$

where $D(C(x,t))$ is the time/depth dependent apparent chloride diffusion coefficient dependent on chloride content $C(x,t)$,

t_m is a time of very long period since diffusion is a slow process which needs longer time to proceed, and C_s is the chloride content of the exposed concrete surface and is a variable dependent on time. To solve the non-linear partial differential equation as given in Eq. (2a), first, the Kirchhoff transformation (Bregbia et al., 1984; Gebhart, 1993; Kane, 1994) was used to render the non-linear problem into a linear one (Sun et al., 2008; Sun et al., 2010; Sun et al., 2012). For the purpose of brevity, the state variable in $C(x,t)$ and $D(C(x,t))$ will be omitted hereinafter. Define new variable ψ in such a way that

$$\frac{d\psi(x,t)}{dC} = D(C) \quad (3)$$

Eq. (3) can also be written in integral form as in the following,

$$\psi(x,t) = \int_{C_R}^C D(C)dC = K(C) \quad (4)$$

The above equation is called Kirchhoff's transformation, where C_R is an arbitrary reference value. For convenience, we take $C_R = C_s$. By applying the concept of chain rule to Eqs. (3) and (4), the following three equation can be obtained, respectively.

$$\frac{\partial \psi}{\partial t} = \frac{\partial \psi}{\partial C} \frac{\partial C}{\partial t} = D \frac{\partial C}{\partial t} \quad (5)$$

$$\frac{\partial \psi}{\partial x} = D \frac{\partial C}{\partial x} \quad (6)$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (7)$$

Eq. (2a) is multiplied by D and changed as

$$D \frac{\partial C}{\partial t} = D \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) - DaD \left(\frac{\partial C}{\partial x} \right) \quad (8)$$

Putting Eqs. (5)-(7) into Eq. (8), we obtain the following linear PDE.

$$\frac{\partial \psi}{\partial t} = D \frac{\partial^2 \psi}{\partial x^2} - Da \frac{\partial \psi}{\partial x} \quad (9a)$$

The initial condition (IC) and boundary condition (BC) stated above are also transferred as

$$IC: \psi(x,0) = K(C=0) = \int_{C_s}^{C=0} D(C)dC = K_0 \quad (9b)$$

$$BC : \psi(0, t) = K(C = C_s) = \int_{C_s}^{C_s} D(C) dC = 0 \quad (9c)$$

$$\psi(x \rightarrow L, t_m) = K(C = 0) = \int_{C_s}^{C=0} D(C) dC = K_0 \quad (9d)$$

By using the method of separation of variable with $\psi(x, t) = X(x)T(t)$, we obtain Eq. (10) from Eq. (9a)

$$XT' = DX^2T - DaXT \quad (10)$$

but we cannot separate function of x and t on opposite sides of this equation. In such a case, it is sometimes helpful to introduce two new functions $U(x, t)$ and $V(x)$, related to $\psi(x, t)$ by

$$\psi(x, t) = U(x, t) + V(x) \quad (11)$$

The idea is to substitute this new expression into the diffusion (or heat) equation and initial and boundary conditions and attempt to choose a proper function of $V(x)$ so that the resulting boundary value problem for $U(x, t)$ can be done by separation of variable or other method such as Laplace's transform.

According to Eq. (11), we have

$$\frac{\partial \psi}{\partial t} = \frac{\partial U}{\partial t} \quad (12a)$$

$$\frac{\partial \psi}{\partial x} = \frac{\partial U}{\partial x} + \frac{\partial V}{\partial x} \quad (12b)$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 V}{\partial x^2} \quad (12c)$$

Inserting Eqs. (11) and (12) into Eq. (9a) to get

$$\frac{\partial U}{\partial t} = \left(D \frac{\partial^2 U}{\partial x^2} - aD \frac{\partial U}{\partial x} \right) + \left(D \frac{\partial^2 V}{\partial x^2} - aD \frac{\partial V}{\partial x} \right) \quad (13)$$

Immediately, this differential equation is simplified if

$$D \frac{\partial^2 V}{\partial x^2} - aD \frac{\partial V}{\partial x} = 0 \quad (14)$$

This is a second order ordinary differential equation (ODE) for $V(x)$ with many solutions. Before choosing one proper solution of $V(x)$, we need consider the boundary conditions being expressed as follows,

$$\psi(0, t) = K(C = C_s) = U(0, t) + V(0) \quad (15)$$

and

$$\psi(x \rightarrow L, t_m) = K(C = 0) = U(x \rightarrow L, t_m) + V(x \rightarrow L) = K_0 \quad (16)$$

Both of these conditions for $U(x, t)$ will be simplified if we choose a valid $V(x)$ such that

$$V(0) = K(C = C_s) = 0; \quad V(L) = K_0 \quad (17)$$

Therefore, we can choose $V(x)$ to be a solution of the following boundary value problem

$$D \frac{\partial^2 V}{\partial x^2} - aD \frac{\partial V}{\partial x} = 0, \quad V(0) = 0, \quad V(L) = K_0 \quad (18)$$

This is a route 2nd order ODE problem to solve. The characteristic equation of Eq. (18) is

$$Dm^2 - Dam = 0 \quad (19)$$

Since $D \neq 0$, we obtain $m = 0$ or $m = a$, Therefore

$$V(x) = C_1 + C_2 e^{ax} \quad (20)$$

where C_1 and C_2 are any arbitrary constants.

Then

$$V(0) = C_1 + C_2 = 0 \quad (21)$$

and

$$V(L) = C_1 + C_2 e^{aL} = K_0 \quad (22)$$

From Eqs. (21) and (22), we obtain the values of C_1 and C_2 by the Cramer rule

$$C_1 = \frac{-K_0}{e^{aL} - 1} \quad \text{and} \quad C_2 = \frac{K_0}{e^{aL} - 1} \quad (23)$$

Thus, choose

$$V(x) = \frac{-K_0}{e^{aL} - 1} + \frac{K_0 e^{ax}}{e^{aL} - 1} \quad (24)$$

With this choice of $V(x)$, $U(x, t)$ satisfies the following equations

$$PDE: \frac{\partial U}{\partial t} = D \frac{\partial^2 U}{\partial x^2} - aD \frac{\partial U}{\partial x} \quad (0 < x < L, \quad t > 0) \quad (25a)$$

$$IC: U(x, 0) = \psi(x, 0) - V(x) = K_0 - X(x) \quad (0 < x < L) \quad (25b)$$

$$BC: U(0, t) = U(L, t) = 0 \quad (25c)$$

We will apply the method of separation of variables and seek a solution of $U(x,t)$. Attempt a solution with the following form:

$$U(x,t) = P(x)Q(t) \tag{26}$$

The substitution of Eq. (26) into Eq. (25) yields

$$PQ' = DP''Q - aDP'Q \tag{27a}$$

or

$$\frac{Q'}{Q} = \frac{DP'' - aDP'}{P} = \lambda \tag{27b}$$

where λ is called a separation constant. We now have

$$DP'' - aDP' - \lambda P = 0 \tag{28}$$

and

$$Q' - \lambda Q = 0 \tag{29}$$

From Eq. (25c), we have

$$U(0,t) = P(0)Q(t) = 0 \tag{30}$$

Since $Q(t) \neq 0$ for all $t > 0$, we have $P(0) = 0$.
From Eq. (25c), we have

$$U(L,t) = P(L)Q(t) = 0 \tag{31}$$

Since $Q(t) \neq 0$ for all $t > 0$, we have $P(L) = 0$.
From Eq. (25b), we know

$$U(x,0) = P(x)Q(0) = K_0 - V(x) \tag{32}$$

Since $P(x) \neq 0$ for $0 < x < L$, we get

$$Q(0) = \frac{K_0 - V(x)}{P(x)}, \quad 0 < x < L \tag{33}$$

At this point, we have two problems for $P(x)$ and $Q(x)$:

$$ODE : P'' - aP' - \frac{\lambda}{D}P = 0 \tag{34a}$$

$$BC : P(0) = P(L) = 0 \tag{34b}$$

and

$$ODE : Q' - \lambda Q = 0 \tag{35a}$$

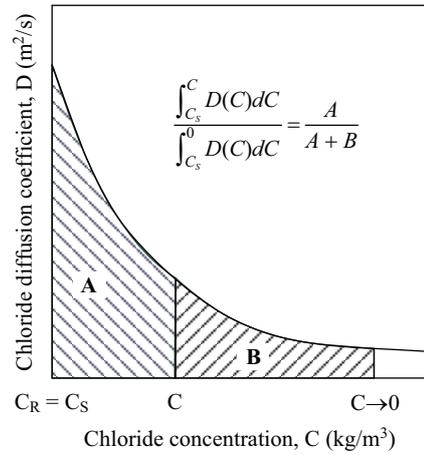


Fig. 1. Area ratio under the D-C curve with the diffusion-migration model.

$$IC : Q(0) = \frac{V(L) - V(x)}{P(x)} \tag{35b}$$

The solution of Eq. (35a) is

$$Q(t) = \alpha e^{\lambda t}, \quad \alpha = \text{constant} \tag{36}$$

Substituting Eq. (35b) into Eq. (36), we have

$$Q(0) = \alpha = \frac{V(L) - V(x)}{P(x)} \tag{37}$$

Thus, the particular solution of Eq. (35) is

$$Q(t) = \frac{V(L) - V(x)}{P(x)} e^{\lambda t} \tag{38}$$

Inserting Eq. (38) into Eq. (26), we obtain

$$U(x,t) = [K_0 - V(x)] e^{\lambda t} \tag{39}$$

Substituting Eq. (24) into Eq. (39), we have

$$U(x,t) = \frac{K_0 (e^{aL} - e^{ax}) e^{\lambda t}}{e^{aL} - 1} \tag{40}$$

It is worthy to point out that Eq. (40) is actually satisfied with the boundary condition of Eq. (25c). Let $x = 0$ into Eq. (40), then $U(0,t) = K_0 e^{\lambda t}$. According to Eq. (9c) and Fig. 1, we have $U(0,t) = 0$. Further, the substitution of $x = L$ into Eq. (40) yields $U(L,t) = 0$.

The substitution of Eqs. (24) and (40) into Eq. (11) yields

$$\psi(x,t) = \frac{K_0 \left[(e^{aL} - e^{ax})e^{\lambda t} + e^{ax} - 1 \right]}{e^{aL} - 1} \quad (41)$$

It is needed to indicate that Eq. (41) is really satisfied with the boundary condition of Eq. (9c). Let $x = 0$ into Eq. (41), then $\psi(0,t) = K_0 e^{\lambda t}$. On the authority of Eq. (9c) and Fig. 1, we know $\psi(0,t) = 0$.

Eq. (41) can be rewritten as

$$\frac{\int_{C_s}^C D(C)dC}{\int_{C_s}^0 D(C)dC} = \frac{(e^{aL} - e^{ax})e^{\lambda t} + e^{ax} - 1}{e^{aL} - 1} \quad (42)$$

Eq. (42) provides the relationships among the apparent diffusion coefficient D , the chloride concentration C , penetration depth x and the time t . The $D(C)$ function was established by the resulting fitting curve. The left side of Eq. (42) is simply the area ratio between areas under the D - C curve from C_s to C and from C_s to 0, as shown in Fig. 1.

3. Chloride Binding Mechanism and Free Chloride

The chloride ions can penetrate into a saturated concrete by ionic diffusion resulting from the existing chloride concentration gradient between the exposed surface and the pore solution of the cement matrix. This process owing to diffusion driving force is generally represented by Fick's first law of diffusion (Martín-Pérez et al., 2000).

$$J_c = -DW_e \frac{\partial C_f}{\partial x} = -\bar{D} \frac{\partial C_f}{\partial x} \quad (43)$$

where J_c is the flux of chloride ions owing to diffusion, D is the time/depth dependent apparent chloride diffusion coefficient dependent on chloride content $C(x,t)$ with the chloride concentration being expressed in kilograms per cubic meter of concrete, \bar{D} is the apparent chloride diffusion coefficient, W_e is the evaporable water content ($W_e = 0.8\%$ (Martín-Pérez et al., 2000)), and $C_f(x,t)$ is the free chloride concentration at depth x and time t .

The relationship among the total, bound, and free chloride concentrations in concrete can be represented as

$$C_t = C_b + W_e C_f \quad (44)$$

where C_t and C_b are the concentration of total and bound chlorides, respectively.

The law of mass conservation for chloride ions in a saturated concrete results in

$$\frac{\partial C_t}{\partial t} = -\frac{\partial J_c}{\partial x} \quad (45)$$

We may assume that W_e to be constant, since we are interested only in the value of D . Putting Eqs. (43)-(45) into Eq. (2a) and using chain rule, we obtain

$$\left(\frac{\partial C_b}{\partial C_f} + W_e \right) \frac{\partial C_f}{\partial t} = -\frac{\partial}{\partial x} \left(-D(C)W_e \frac{\partial C_f}{\partial x} \right) - D(C)W_e a \frac{\partial C_f}{\partial x} \quad (46)$$

where $\frac{\partial C_b}{\partial C_f}$ is the binding capacity of the concrete binder (m^3 of pre solution/ m^3) of concrete as defined by Nilsson et al. (1994).

Eq. (46) can be rewritten as

$$\frac{\partial C_f(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(D^*(C(x,t)) \frac{\partial C_f(x,t)}{\partial x} \right) - D^*(C(x,t)) a \frac{\partial C_f(x,t)}{\partial x} \quad (47a)$$

with

$$D^* = \frac{D(C(x,t))}{1 + \frac{1}{W_e} \frac{\partial C_b}{\partial C_f}} \quad (47b)$$

The associated initial and boundary conditions of Eq. (47a) become

$$C_f(x,0) = 0 \quad (47c)$$

$$C_f(0,t) = C_s \quad (47d)$$

$$C_f(x \rightarrow L, t_m) = 0 \quad (47e)$$

By applying the same method mentioned before, the analytical solution of Eq. (47) yields

$$\frac{\int_{C_s}^{C_f} D^*(C)dC}{\int_{C_s}^0 D^*(C)dC} = \frac{(e^{aL} - e^{ax})e^{\lambda t} + e^{ax} - 1}{e^{aL} - 1} \quad (48)$$

4. Chloride Binding Isotherm

The chloride binding isotherm is defined as the depicted relationship between the bound and free chloride concentrations in concrete under a given temperature condition. Eq. (47b) indicates the apparent chloride diffusion coefficient and the corresponding binding isotherm. Four theoretical curves used in the literature to express chloride binding isotherm in concrete are reviewed in the following (Martín-Pérez et al., 2000):

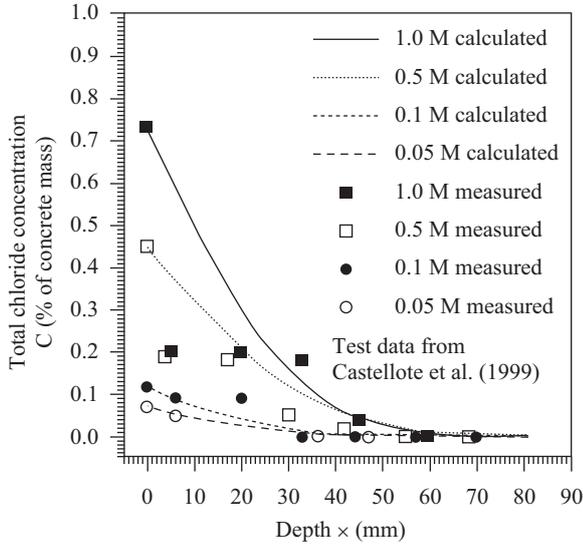


Fig. 2. Total chloride profiles at different chloride concentrations.

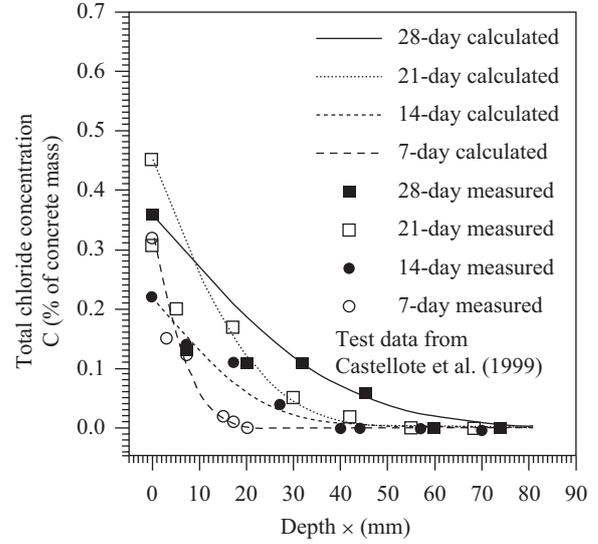


Fig. 3. Total chloride profiles at different times.

(1) No binding isotherm

$$C_b = 0, \frac{\partial C_b}{\partial C_f} = 0, D^* = D \quad (49)$$

(2) Linear binding isotherm

$$C_b = \alpha C_f, \frac{\partial C_b}{\partial C_f} = \alpha, D^* = \frac{D}{1 + \frac{\alpha}{W_e}} \quad (50)$$

where α is the binding constant.

(3) Langmuir binding isotherm

$$C_b = \frac{\alpha C_f}{1 + \beta C_f}, \frac{\partial C_b}{\partial C_f} = \frac{\alpha}{(1 + \beta C_f)^2}, D^* = \frac{D}{1 + \frac{\alpha}{W_e (1 + \beta C_f)^2}} \quad (51)$$

where α and β are the binding constants.

(4) Freundlich binding isotherm

$$C_b = \alpha C_f^\beta, \frac{\partial C_b}{\partial C_f} = \alpha \beta C_f^{\beta-1}, D^* = \frac{D}{1 + \frac{\alpha \beta}{W_e} C_f^{\beta-1}} \quad (52)$$

where α and β are the binding constants.

Substituting the values of C_s and D^* represented by Eqs. (49)-(52) into Eq. (48), we can obtain the free chloride concentration at depth x and time t of the analytical solution of one-dimensional time/depth dependent diffusion-migration PDE.

III. RESULTS AND DISCUSSION

Based on $\alpha = -1$, $F = 96500 \text{ J}/(\text{mole} \cdot V)$, $R = 8.314 \text{ J}/(\text{mole} \cdot K)$, $T = 298K$, $L = 0.15 \text{ m}$, $E = -\frac{\Delta V}{L} = -\frac{12V}{0.15m} = -80V/m$, we calculate $a = \frac{zFE}{RT} = 3115.95 \text{ 1/m}$.

According to the data measured by Castellote et al. (1999) and using Eq. (42), Fig. 2 shows the total chloride profiles at different chloride concentrations. Values of chlorides at $x = 0$ show the surface concentration. It generally resulted in such a quantity higher than the rest of the profile. It is obvious that the calculated results are in agreement with the measured data (Castellote et al., 1999) for the chloride concentrations 0.05 M and 0.1 M while the calculated results are not consisted with the measured data (Castellote et al., 1999) for the chloride concentrations 0.5 M and 1 M. Fig. 3 indicates the total chloride profiles at different times. It is understandable that the calculated results are agreeable with the measured data (Castellote et al., 1999) at different times. Based on the data measured by Castellote et al. (1999) and using Eq. (48), Fig. 4 displays the free chloride profiles at different chloride concentrations. It is clear that the calculated results are in accordance with the measured data (Castellote et al., 1999) for the chloride concentrations 0.05 M and 0.1 M whereas the calculated results are not agreeable with the measured data (Castellote et al., 1999) for the chloride concentrations 0.5 M and 1 M. Fig. 5 illustrates the free chloride profiles at different times. It is perceptible that the calculated results are in agreement with the measured data (Castellote et al., 1999) at 14 days and 28 days while the calculated results are not agreeable with the measured data (Castellote et al., 1999) at 7 days and 21 days.

According to the values of $C_s = 0.45M$ (see Fig. 2), $a = 3115.95 \text{ 1/m}$, $\alpha = 0.19$ (linear binding), $\alpha = 0.98$, $\beta = 0.29$

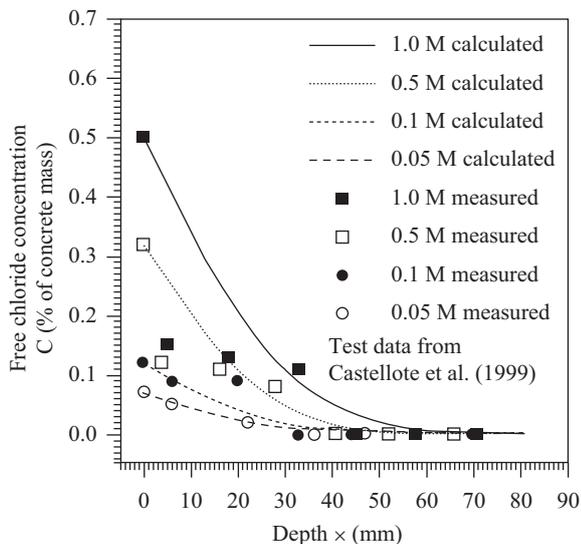


Fig. 4. Free chloride profiles at different chloride concentrations.

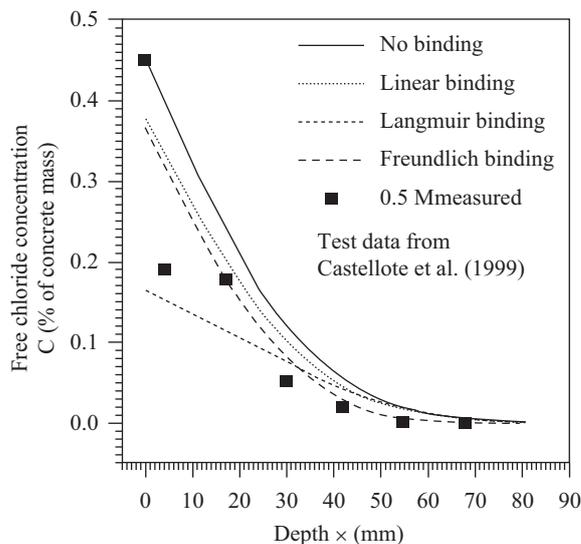


Fig. 6. Free chloride profiles by different chloride-binding isotherm calculations.

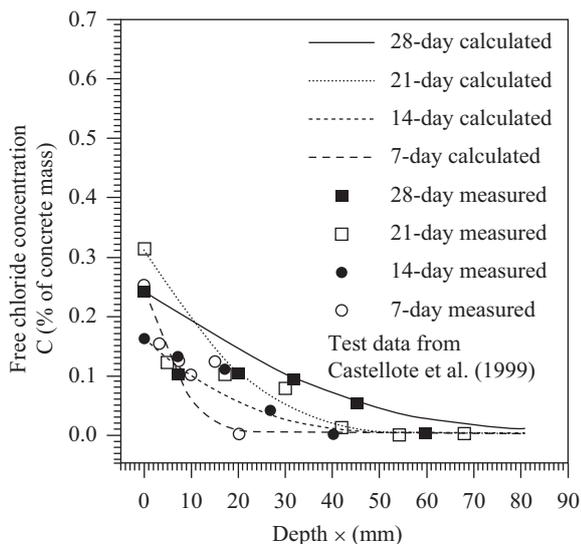


Fig. 5. Free chloride profiles at different times.

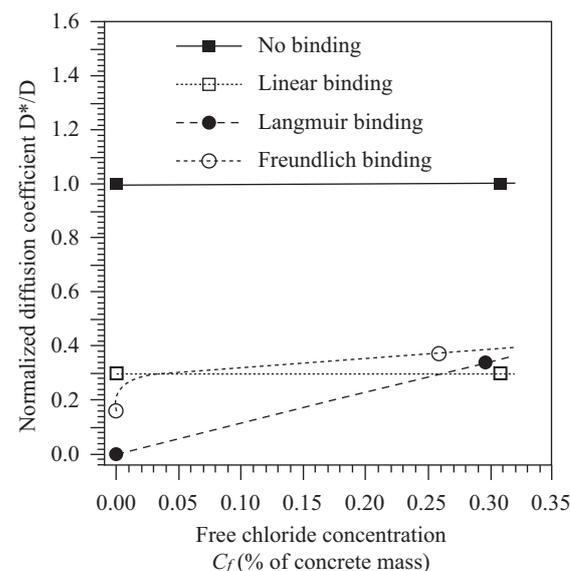


Fig. 7. The effect of chloride binding on the diffusivity under external $[NaCl] = 0.5 M$.

(Langmuir binding), $\alpha = 1.03$, $\beta = 0.36$ (Freundlich binding) (Martín-Pérez et al., 2000) and using the measured data with an external concentration $[NaCl] = 0.5M$ (Castellote et al., 1999), and substituting Eqs. (49)-(52) into Eq. (50), we obtain the results as shown in Fig. 6. From Fig. 6, the calculated results obtained by the Freundlich binding isotherm is in a better agreement with those of measured data (Castellote et al., 1999). It is worthy of pointing out that the calculated results predicted by the no binding isotherm is not quite agreeable with those of measured data.

The effect of chloride binding in Eq. (47b) is to diminish the diffusivity of chloride ions in concrete which represents the binding capacity of the specific binder as shown in Fig. 7. For measurement of ignoring binding or considering a linear

binding isotherm, the diffusivity D^* is constant as chlorides penetrate into the concrete. Nevertheless, when the non-linearity is considered in the bound-free chloride relation, D^* will vary through the concrete depth, which reflects the chloride binding capacity of the concrete binder on the levels of chloride ions in the pore solution (Nilsson et al., 1994). As the values of C_f less than 0.3% mass of concrete, the values of D^*/D of the Freundlich isotherm is higher than that of Langmuir isotherm while as the values of C_f greater than 0.3% mass of concrete, the value of D^*/D of the Freundlich isotherm is approximately close to that of the Langmuir isotherm.

According to the curve of the free chloride concentration

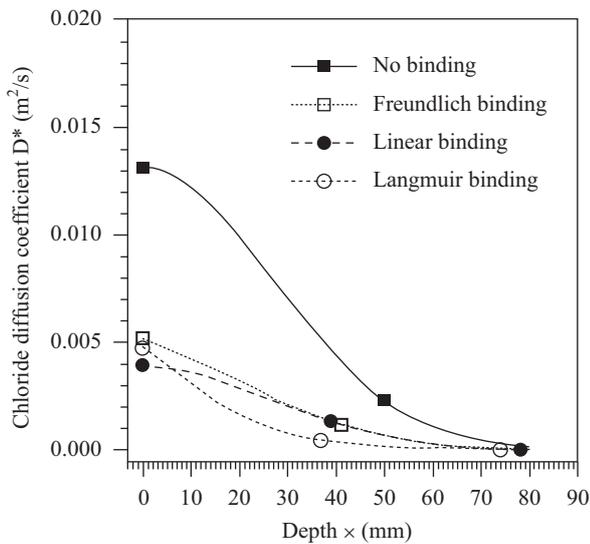


Fig. 8. Chloride diffusion coefficient D^* (m^2/s) with different chloride-binding isotherm calculations.

versus depth under an external concentration of 0.5 M NaCl (Castellote et al., 1999) and substituting Eqs. (49)-(52) into Eq. (48), we may obtain the effect of chloride diffusivity by different chloride-binding isotherm calculations on penetration depth as shown in Fig. 8. It is obvious that the chloride diffusivities are all decreased when the concrete depth is increased. Fig. 8 shows the values of diffusivity predicted by no binding, linear binding, Langmuir isotherm, and Freundlich isotherms are 0.0128, 0.0038, 0.0036, and 0.0047 m^2/s at $x = 7$ mm and 0.0062, 0.0002, 0.007 and 0.002 m^2/s at $x = 33$ mm, respectively. The order of reduction amount of diffusivity from large to small is described as follows: (1) no binding isotherm, (2) Freundlich binding isotherm (3) linear binding isotherm, and (4) Langmuir binding isotherm.

IV. CONCLUSIONS

The approach to obtaining the analytical solution of one-dimensional non-steady-state diffusion-migration equation by the Kirchhoff transformation technique in conjunction with the method of separation of variable has been described and the resulting outcomes were compared satisfactorily with the previously published experimental data. Some important conclusions are drawn as follows:

1. This proposed method allows the predictions of chloride profiles, considering the non-steady-state and non-constant diffusion coefficients dependent on both time and penetration depths, by just using the experimental data of some diffusion migration tests with a short period of test time.
2. Obviously, different chloride binding isotherms can be easily implemented into the currently proposed non-steady diffusion-migration model. It has been clearly shown that four different chloride binding isotherms with distinct chloride

bindings and chloride depths investigated in this study apparently have significant effects on the chloride profile of porous concrete. Because both the increase of chloride binding in the interior of concrete and the increase of ingress depth of chloride ion from the exposed concrete surface tend to reduce the chloride diffusivity of concrete, it is found that the ranking of reduction amount of chloride diffusivities from large to small is expressed as in the following order: (1) no binding isotherm, (2) Freundlich binding isotherm, (3) Linear binding isotherm, and (4) Langmuir binding isotherm.

3. An extensive laboratory investigations are certainly needed to tune the proposed diffusion-migration model as well as an extension of this model to include other effects of additional parameters like the W/C ratio of concrete, the concrete porosity, and material properties of mixing constituents of concrete, etc.

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