TIME/DEPTH DEPENDENT DIFFUSION-COVECTION MODEL OF CHLORIDE WITH TRANSPORTATION IN CONCRETE STRUCTURES WITH CHLORIDE-BINDING ISOTHERMS

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ABSTRACT

Ion transport through a hydrated cement system often becomes a principal factor to degrade concrete in a chloride-laden environments. Based on the transport mechanism of chloride ion, an analytical solution of mathematical model for predicting chloride penetration into concrete structures was herein derived. The model consists of both the diffusion of chloride due to concentration gradient and the convection of chloride due to moisture transport. The model also depends on temperature, age, relative humidity, and chloride binding. Based on both the diffusion coefficient and the mean velocity with time/depth dependence, an analytical solution of the mathematical model developed by previous researchers was solemnly derived and used to predict the properties of concrete structures contaminated by chloride. The chloride penetration decreases as the time-dependence ratio increases. The amount of chloride accumulated in concrete increases as the relative humidity increases. Moreover, the proposed model may be effectively used for the practical evaluation and design for durability of concrete structures.

I. INTRODUCTION

Reinforced concrete (RC) structures have been actively built in aggressive environment in numerous countries. The RC structures cannot escape completely from corrosion, particu-

larly when they are generally subjected to chloride attack due to seawater or de-icing salt. Chloride-induced corrosion is one of the primary causes of serviceability problems (staining, cracking, spalling or delamination of concrete) of such concrete structures (Martín-Pérez et al., 2001; Oh and Jang, 2003a, 2003b, 2004; Darmawan, 2010). Accordingly, chloride-induced corrosion is the most important durability issue in a RC structure (Yuan et al., 2011). Moreover, the resistance to chloride penetration becomes very momentous in the design and construction of concrete structures (Oh and Jang, 2003a).

Swatekitithan (2004) studied the transport mechanism of chloride, especially concentrating on the effect of wetting-drying conditions on the penetration. He pointed out that the penetration of chloride ion into concrete is owing to two major mechanisms; the diffusion process caused by concentration gradient of chlorides, and advective transport due to bulk suction of pore water. It is worthy to point out that the moisture content or relative humidity inside concrete undergone an ambient environment, such as complicated wetting-drying condition, does not have constant distribution throughout the depth. Conciatori et al. (2008) investigated that chloride ions migrate rapidly into the concrete cover during precipitation periods with and without the presence of deicing salt. Seasonal variation can meaningfully affect chloride ion profiles. Owing to the meaningful chloride ion transport towards larger depth in the concrete, chloride ion profiles may indicate meaningful concentrations at the steel reinforcement level during winter periods and diminished concentrations in summer. The space variability of the moisture content reveals miscellaneously depending on the type of contact with water (exposure to stagnant or splash water) or water vapor (mist exposure). This has a direct shock on the chloride ion convection by water. The influences of chloride ion on RC structures have led to miscellaneous studies on chloride and structures in aggressive environment. The analytical solution of Fick's second law of linear diffusion in combination with initial and boundary conditions for semi-infinite concrete is a good approximation of

the chloride penetration into concrete (Collerpardi et al., 1972; Crank, 1975). The apparent diffusivity can be inversely calculated from the chloride concentration profiles of the core taken from existing concrete structures or the specimens tested in the laboratory by means of curve-fitting of analytical solution. The values of diffusivity so calculated are usually used to prophesy of the penetration depth of chloride in concrete during longer periods. Though this method is widely employed, the chloride penetration into concrete is a much more complicated phenomenon for many explanations: (1) The diffusivity is not a constant parameter, but varies with age, temperature, porosity and relative humidity. (2) The chloride binding is of a notable effect on chloride penetration. Only free chloride can diffuse into bulk concrete. (3) Convection flow of chloride ions as well as chloride diffusion is of a critical role in moving the chloride ions in concrete, particularly when exposed to wetting-drying condition. The boundary conditions are also much more complex to simulate the real exposure conditions. Oh and Jang (2007) studied that chloride transport in concrete is considered both the diffusion by chloride concentration and the convection by moisture transport and that linear chloride binding is also considered. They also used the finite element technique to obtain the numerical solutions for laboratory and field conditions. They found that the convection by moisture transport can accelerate the chloride penetration into concrete and can cause the accumulation of chloride near the concrete surface. To date, however, no studies have attempted to derive the analytical solution of the mathematical model developed by Oh and Jang (2007). This is a notable shortcoming, because the use of finite element technique in previous studies may have resulted in under- or over-estimation of the properties of concrete structures exposed in chloride environments.

The main objective of this paper is seriously to derive an analytical solution of the mathematical model suggested by Oh and Jang (2007) and to use it for predicting the properties of concrete structures contaminated by chloride. The predicted results obtained from proposed method are compared with those results measured by Oh and Jang (2007). The present study results may provide as an engineering reference of decision making for the quantity evaluation of concrete structures.

II. MATHEMATICAL MODEL FORMULATION

1. Chloride Transport and Binding

Considering the chloride diffusion and the convection by moisture transport in concrete, the chloride flux can be expressed as

$$J_c = -D_c \frac{\partial C_f}{\partial x} + \bar{u} \, C_f \qquad (1)$$

where J_c is the chloride flux [$\mathrm{kg/(s \cdot m^2)}$], D_c is the intrinsic

chloride diffusion coefficient ($\mathrm{m^2/s}$), C_f is the free chloride concentration [$\mathrm{kg/m^3}$ of pore solution], x is the depth [m], and $\bar{u}$ is the mean velocity of moisture transport in concrete [m/s].

According to the equation of mass balance (Crank, 1975), the one-dimensional chloride transport in concrete can be stated as

$$\frac{\partial C_t}{\partial t} = -\frac{\partial J_c}{\partial x} \qquad (2)$$

where C_t is the total chloride concentration of concrete [$\mathrm{kg/m^3}$ of concrete] and t is the time [s].

Substituting Eq. (1) into Eq. (2), we obtain

$$\frac{\partial C_t}{\partial t} = \frac{\partial}{\partial x}\left(D_c \frac{\partial C_f}{\partial x}\right) - \frac{\partial\left(\bar{u} C_f\right)}{\partial x} \qquad (3)$$

The relationship among total, bound, and free chloride concentrations in concrete can be described by

$$C_t = C_b + C_f \qquad (4)$$

where C_b is the bound chlorides concentration [$\mathrm{kg/m^3}$ of concrete].

Taking derivative with respect to t and using the chain rule to Eq. (4), we have

$$\frac{dC_f}{dC_t} = \frac{1}{1 + \dfrac{dC_b}{dC_f}} \qquad (5)$$

where $\dfrac{dC_f}{dC_t}$ is called the chloride binding capacity and $\dfrac{dC_b}{dC_f}$ is called the chloride binding isotherm (Xi and Bažant, 1999).

Putting Eq. (4) into Eq. (3) and using the chain rule, we have

$$\left(1 + \frac{\partial C_b}{\partial C_f}\right)\frac{\partial C_f}{\partial t} = \frac{\partial}{\partial x}\left(D_c \frac{\partial C_f}{\partial x}\right) - \frac{\partial\left(\bar{u} C_f\right)}{\partial x} \qquad (6)$$

If the term of $1 + \dfrac{\partial C_b}{\partial C_f}$ is only a function of t, which is a constant with respect to x, then Eq. (6) can be written in terms of

$$\frac{\partial C_f}{\partial t} = \frac{\partial}{\partial x}\left(D_c^* \frac{\partial C_f}{\partial x}\right) - \frac{\partial\left(\bar{u}^* C_f\right)}{\partial x} \qquad (7)$$

where

$$D_c^* = \frac{D_c}{1 + \dfrac{\partial C_b}{\partial C_f}} \qquad (8)$$

and
$$\bar{u}^* = \frac{\bar{u}}{1 + \dfrac{\partial C_b}{\partial C_f}} \qquad (9)$$

2. Moisture Transport

The moisture mass balance equation without sink or source term (e,g., self-desiccation) can be expressed as

$$\frac{\partial \theta}{\partial t} = -\frac{\partial J_\theta}{\partial x} \qquad (10)$$

where θ is the moisture content in unit weight of concrete [kg/kg of concrete], and J_θ is the moisture flux [m/s] brought about moisture diffusion and capillary suction. The moisture flux, J_θ, can be presented in terms of (Oh and Jang, 2003a)

$$J_\theta = \theta \bar{u} = -D_\theta \frac{\partial \theta}{\partial x} \qquad (11)$$

where D_θ is the moisture diffusion coefficient [m²/s].

The substitution of Eq. (11) into Eq. (10) yields

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left(D_\theta \frac{\partial \theta}{\partial x}\right) \qquad (12)$$

On the basis of Eq. (11), the mean velocity of moisture flow can be expressed as

$$\bar{u} = -\frac{D_\theta}{\theta}\frac{\partial \theta}{\partial x} \qquad (13)$$

3. Chloride Diffusivity in Concrete

In the real situation of chloride diffusivity in concrete, the previous researches (Mangat and Molloy, 1994; Kropp and Hilsdort, 1995; Tang, 1996) have indicated that the chloride diffusivity in concrete is a function of numerous factors such as porosity, degree of hydration, temperature, aggregate size, relative humidity and local chloride concentration. In the present mathematical model, the dependences of the chloride diffusion coefficient were estimated using the multifactor method (Saetta et al., 1993; Oh and Jang, 2007) as follows:

$$D_c = D_c^R f_T(T) f_t(t) f_h(h) \qquad (14)$$

where D_c^R is the measured diffusion coefficient for some defined reference conditions, and $f_T(T)$, $f_t(t)$ and $f_h(h)$ are the factors describing the dependences of D_c on temperature (T), age (t) and pore relative humidity (h), which can be defined, respectively, by Eqs. (15), (16) and (17) (Bažant and Thonguthai, 1978; Bažant, 1979).

$$f_T(T) = \exp\left[\frac{U}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \qquad (15)$$

where T_0 is the reference temperature [K] for D_c^R, T is the temperature [K] at time t, U is the diffusion activation energy [kJ/mol], and R is the gas constant [kJ/(mol · K)].

$$f_t(t) = \kappa + (1-\kappa)\left(\frac{t_0}{t}\right) \qquad (16)$$

where κ is the coefficient defined as the ratio between the diffusion coefficient for $t \to \infty$ and the diffusion coefficient for $t = t_0$ (reference time), which varies from 0 to 1 according to Saetta et al. (1993).

$$f_h(h) = \lambda + \frac{1-\lambda}{1 + \left(\dfrac{1-h}{1-h_c}\right)^4} \qquad (17)$$

where h_c is the critical relative humidity ($h_c = 0.75$ for 25°C), λ is a constant ($\lambda \cong 0.25$ for 25°C) (Mangat and Molloy, 1994). Here, based on the sorption and desorption isotherm (Bažant and Najjar, 1971; Bažant and Thonguthai, 1978), the pore relative humidity is simplified as

$$h = \frac{\theta}{\theta_{sat}} \qquad (18)$$

where θ_{sat} is the saturated moisture constant in unit weight of concrete [kg/kg].

4. Chloride Binding Isotherms

Chloride binding isotherm presents the relationship between free and bound chloride in concrete at a given temperature. They are dependent on the components making up that system such as C_3A concrete, pH of the pore solutions, and supplementary cementing materials. They are also dependent on the environmental conditions such as temperature and relative humidity.

Eq. (8) describes the apparent diffusion coefficient and the corresponding chloride binding isotherm. Four theoretical curves used in the literature to express chloride binding isotherm in concrete are reviewed in the following manner (Martín-Pérez et al., 2000):

No binding

$$C_b = 0, \quad \frac{\partial C_b}{\partial C_f} = 0, \quad D_c^* = D_c \qquad (19)$$

Linear binding

$$C_b = \alpha C_f, \quad \frac{\partial C_b}{\partial C_f} = \alpha, \quad D_c^* = \frac{D_c}{1+\alpha} \qquad (20)$$

where α is the isotherm parameter.
Langmuir isotherm

$$C_b = \frac{\alpha C_f}{1+\beta C_f}, \quad \frac{\partial C_b}{\partial C_f} = \frac{\alpha}{\left(1+\beta C_f\right)^2}, \quad D_c^* = \frac{D_c}{1+\dfrac{\alpha}{\left(1+\beta C_f\right)^2}} \tag{21}$$

where α and β are the isotherm parameters, which depend on both C-S-H intrinsic properties and pH of the pore solution.
Freundlich isotherm

$$C_b = \alpha C_f^{\beta}, \quad \frac{\partial C_b}{\partial C_f} = \alpha\beta C_f^{\beta-1}, \quad D_c^* = \frac{D_c}{1+\alpha\beta C_f^{\beta-1}} \tag{22}$$

where α and β are the isotherm parameters, which depend on both C-S-H intrinsic properties and are thus independent of mix-composition and age.

5. Analytical Solution

Oh and Jang (2007) considered linear chloride binding isotherm (see Eq. (20)). Thus, the substitution Eq. (20) into Eq. (4) yields

$$C_t = C_b + C_f = \alpha C_f + C_f = \left(1+\alpha\right) C_f = \gamma\, C_f, \tag{23}$$

where the chloride binding capacity, $\dfrac{C_f}{C_t} = \dfrac{1}{1+\alpha} = \dfrac{1}{\gamma}$, is to be assumed. Based on Eq. (7), we have the one-dimensional time/depth dependent diffusion-convection partial differential equation (PDE) together with initial and boundary conditions for a solid can be written as

$$\text{PDE} \quad \frac{\partial C_f}{\partial t} = \frac{\partial}{\partial x}(D_c^* \frac{\partial C_f}{\partial x}) - \frac{\partial}{\partial x}(\bar{u}^* C_f) \tag{24a}$$

$$\text{IC} \quad C_f(x,0) = C_i \tag{24b}$$

$$\text{BC} \quad C_f(0,t) = C_s \tag{24c}$$

$$C_f(x \to \infty, t_m) = C_{fi} \tag{24d}$$

where, $t(s)$ is the exposure period, $t_m(s)$ is a large number of time period, C_i is the initial chloride concentration of the concrete structures, C_s is the surface concentration, and C_{fi} is the final chloride concentration.

In order to solve the diffusion-convection problem of chloride in concrete structures modeled by Eqs. (24a)-(24d), first of all we assume (Liang and Lin, 2003)

$$C_f(x,t) = e^{\rho x + \sigma t} \phi(x,t) \tag{25}$$

where $e^{\rho x + \sigma t}$ is the exponential function, ρ and σ are the constant parameters, and $\phi(x,t)$ is a new function of chloride concentration.

The substitution of Eq. (25) into Eq. (24) yields

$$\text{PDE} \quad \frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x}(D_c^* \frac{\partial \phi}{\partial x}) - \frac{\sigma}{2}\phi \tag{26a}$$

$$\text{IC} \quad \phi(x,0) = e^{-\rho x} C_i \tag{26b}$$

$$\text{BC} \quad \phi(0,t) = e^{-\sigma t} C_s \tag{26c}$$

$$\phi(x \to \infty, t) = e^{-\rho x - \sigma t} C_{fi} \tag{26d}$$

We again assume (Liang and Lin, 2003; Sun et al., 2012)

$$\phi(x,t) = e^{-\frac{\sigma}{2}t}\bar{\phi}(x,t) \tag{27}$$

where $\bar{\phi}(x,t)$ is a new function of chloride concentration.
Inserting Eq. (27) into Eq. (26), we have

$$\text{PDE} \quad \frac{\partial \bar{\phi}}{\partial t} = \frac{\partial}{\partial x}(D_c^* \frac{\partial \bar{\phi}}{\partial x}) \tag{28a}$$

$$\text{IC} \quad \bar{\phi}(x,0) = e^{-\rho x + \frac{\sigma}{2}t} C_i \tag{28b}$$

$$\text{BC} \quad \bar{\phi}(0,t) = e^{-\frac{\sigma}{2}t} C_s \tag{28c}$$

$$\bar{\phi}(x \to \infty, t) = e^{-\rho x - \frac{\sigma}{2}t} C_{fi} \tag{28d}$$

Eq. (28a) is a non-linear PDE. To solve this equation, first, the Kirchhoff transformation is used to render the non-linear problem into a linear one (Sun et al., 2008; 2010; 2012). A new variable ψ is defined such that

$$\frac{d\psi(x,t)}{d\bar{\phi}} = D_c^*(\bar{\phi}) \tag{29}$$

Eq. (29) can also be written in integral form as in the following:

$$\psi(x,t) = \int_{\bar{\phi}_{sm}}^{\bar{\phi}_r} D_c^*(\bar{\phi})d\bar{\phi} = K(\bar{\phi}_r) = K_r \tag{30}$$

where $\bar{\phi}_r$ is an arbitrary reference value of concentration, $\bar{\phi}_{sm}$ is a nominal chloride surface concentration at t_m, and Eq. (30) is called the Kirchhoff transformation. By applying the concepts of chain rule and Leibniz's rule to Eqs. (29) and (30), the

following three equations can be obtained, respectively.

$$\frac{\partial \psi}{\partial t} = \frac{\partial \psi}{\partial \overline{\phi}} \frac{\partial \overline{\phi}}{\partial t} = D_c^* \frac{\partial \overline{\phi}}{\partial t} \quad (31)$$

$$\frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial \overline{\phi}} \frac{\partial \overline{\phi}}{\partial x} = D_c^* \frac{\partial \overline{\phi}}{\partial x} \quad (32)$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial}{\partial x}\left(D_c^* \frac{\partial \overline{\phi}}{\partial x} \right) \quad (33)$$

Eq. (28a) is multiplied by D_c^* and changed as

$$D_c^* \frac{\partial \overline{\phi}}{\partial t} = D_c^* \frac{\partial}{\partial x}(D_c^* \frac{\partial \overline{\phi}}{\partial x}) \quad (34)$$

Putting Eqs. (31)-(33) into Eq. (34), we obtain the following linear PDE

$$\frac{\partial \psi}{\partial t} = D_c^* \frac{\partial^2 \psi}{\partial x^2} \quad (35a)$$

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

$$IC : \psi(x,0) = K(\overline{\phi}_i = e^{-\rho x + \frac{\sigma}{2}t} C_i) = \int_{\overline{\phi}_{sm}}^{\overline{\phi}_i} D_c^*(\overline{\phi})d\overline{\phi} = K_i \quad (35b)$$

$$BC : \psi(0,t) = K(\overline{\phi}_s = e^{-\frac{\sigma}{2}t} C_S) = \int_{\overline{\phi}_{sm}}^{\overline{\phi}_s} D_c^*(\overline{\phi})d\overline{\phi} = K_s \quad (35c)$$

$$\psi(x \to \infty, t) = K(\overline{\phi}_{fi} = e^{-\rho x - \frac{\sigma}{2}t} C_{fi}) = \int_{\overline{\phi}_{sm}}^{\overline{\phi}_{fi}} D_c^*(\overline{\phi})d\overline{\phi} = K_{fi} \quad (35d)$$

The Laplace transformation (O'Neil, 2011) is used to solve Eq. (35). The definition for the Laplace transformation of $\psi(x,t)$ is given as

$$\Omega(x,s) = L\left[\psi(x,t)\right] = \int_0^\infty \psi(x,t)e^{-st}dt \quad (36)$$

Thus, the solution of Eq. (35) through the Laplace transformation is given as follows:

$$\Omega(x,s) = \frac{K_i}{s} + (K_s - K_{fi})\frac{e^{-\sqrt{\frac{s}{D_c^*}}x}}{s} \quad (37)$$

Since (Carslaw and Jaeger, 1959)

$$L^{-1}\left\{ \frac{e^{-\sqrt{\frac{s}{D_c^*}}x}}{s} \right\} = 1 - erf\left(\frac{x}{\sqrt{4D_c^*t}}\right) = erfc\left(\frac{x}{\sqrt{4D_c^*t}}\right) \quad (38)$$
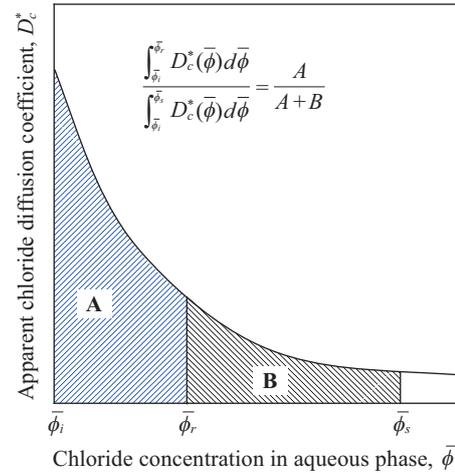
Fig. 1. Area ratio under the $D_c^* - \overline{\phi}$ curve for interpreting the geometric meaning of Eq. (40).

where *erf* and *erfc* are the error and complementary error functions, respectively,

Thus, by taking the inverse Laplace transformation (Carslaw and Jaeger, 1959) of Eq. (37) we have

$$\psi(x,t) = K_i + (K_s - K_{fi})erfc\left(\frac{x}{\sqrt{4D_c^*t}}\right) \quad (39)$$

The substitution of Eqs. (30), (35b), (35c) and (35d) into Eq. (39) yields

$$\frac{\int_{\overline{\phi}_{sm}}^{\overline{\phi}_r} D_c^*(\overline{\phi})d\overline{\phi} - \int_{\overline{\phi}_{sm}}^{\overline{\phi}_i} D_c^*(\overline{\phi})d\overline{\phi}}{\int_{\overline{\phi}_{sm}}^{\overline{\phi}_s} D_c^*(\overline{\phi})d\overline{\phi} - \int_{\overline{\phi}_{sm}}^{\overline{\phi}_{fi}} D_c^*(\overline{\phi})d\overline{\phi}} = \frac{\int_{\overline{\phi}_i}^{\overline{\phi}_r} D_c^*(\overline{\phi})d\overline{\phi}}{\int_{\overline{\phi}_{fi}}^{\overline{\phi}_s} D_c^*(\overline{\phi})d\overline{\phi}}$$

$$= erfc\left(\frac{x}{\sqrt{4D_c^*t}}\right) \quad (40)$$

It is needed to point out that $\overline{\phi}_i$ is equal to $\overline{\phi}_{fi}$ due to Eqs. (35c) and (35d) in the process of the Laplace transformation. Eq. (40) offers the relationships among the apparent diffusion coefficient D_c^*, the new free chloride concentration $\overline{\phi}$, penetration depth *x*, and time *t*. The free apparent chloride diffusion coefficients D_c^* varied with depth *x* and time *t* according to experimental results. The $D_c^*(\overline{\phi})$ function was established by the resulting fitting curve. The left side of Eq. (40) is simply the area ratio between areas under the $D_c^* - \overline{\phi}$ curve from $\overline{\phi}_i$ to $\overline{\phi}_r$ and from $\overline{\phi}_i$ to $\overline{\phi}_s$, shown in Fig. 1.

6. Fick's Second Law of Diffusion

The diffusion mechanism of chloride transport behavior in

concrete is dependent on the concentration of chloride. The concentration of chloride can be calculated by using a diffusion equation which assumes that chemical reactions are neglected. The apparent diffusion coefficient, D_{ca}, of chloride is defined by Fick's second law for a semi-infinity medium with constant chloride exposure:

$$\frac{\partial C}{\partial t} = D_{ca} \frac{\partial^2 C}{\partial x^2}, \quad D_{ca} = \text{constant} \tag{41a}$$

$$C(x,0) = 0 \tag{41b}$$

$$C(0,t) = C_s \tag{41c}$$

$$C(x \to \infty, t) = 0 \tag{41d}$$

where $C(x,0)$ is the chloride concentration at depth x at time t, C_s is the surface concentration of chloride on concrete, and D_{ca} is the apparent diffusion coefficient of chloride.

Applying the Laplace transformation (Sun et al., 2010) to Eq. (41), the analytical solution (Carslaw and Jaeger, 1959; Crank, 1975) of Eq. (41) is obtained

$$C(x,t) = C_s \, erfc \left(\frac{x}{\sqrt{4D_{ca}t}} \right) \tag{42}$$

where *erfc* is the complementary error function.

III. RESULTS AND DISCUSSION

In order to verify the proposed model mentioned above, data of the field and the laboratory test measurement worked by Oh and Jang (2007) were used as input parameters. According to Eqs. (23), (40), and (42) and using the commercial software programmed "Mathematica" (2013), we may make some pictures to foretell the properties of concrete contaminated by chloride. Now some results are illustrated in the following.

1. Effect of Cement Type

Fig. 2 shows that the predicted chloride profiles are compared with the laboratory test specimens worked by Oh and Jang (2007). Fig. 2 displays that the predicted values are in good agreement with test data for chloride penetration. Based on Fig. 2 it is extremely obvious that the diffusion coefficients of Type I cement mixtures are generally smaller than those of Type V cement mixtures. This reason is possibly the different binding effects of different types of cement. The C_3A contents generally affect the binding capacity. The C_3A content of Type I cement is higher than Type V cement. Based on Fig. 2, it is also clearly seen that the supplement of fly ash into concrete makes less the diffusion coefficients about 15-50%. This leads to the less penetration depth of chloride ions into concrete
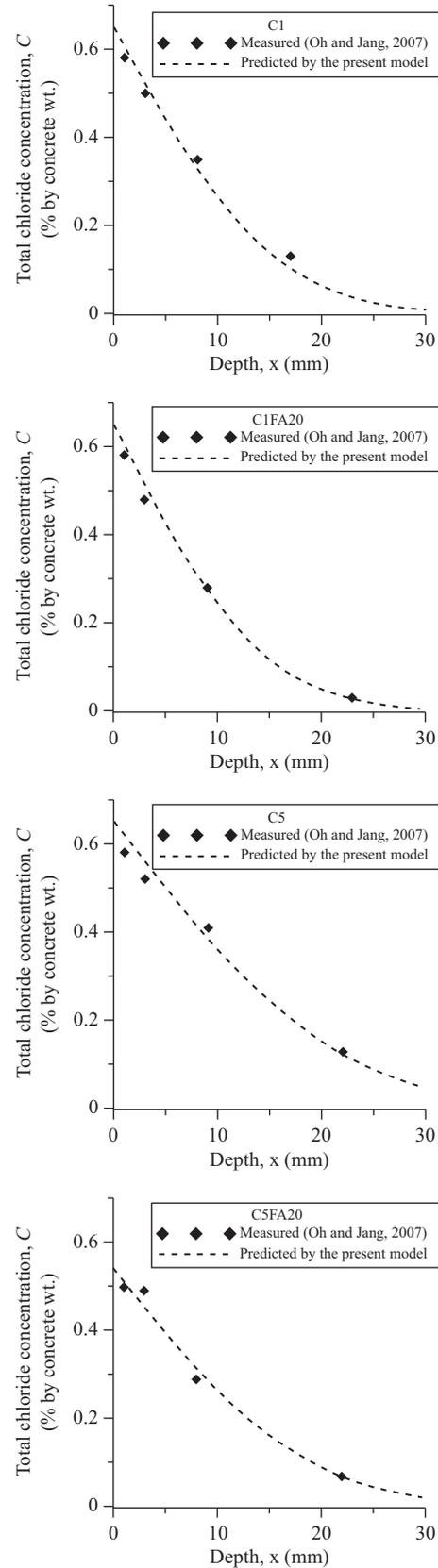
Fig. 2. **Comparison of predicted and measured chloride profiles for specimens with different mixture proportions in laboratory conditions.**
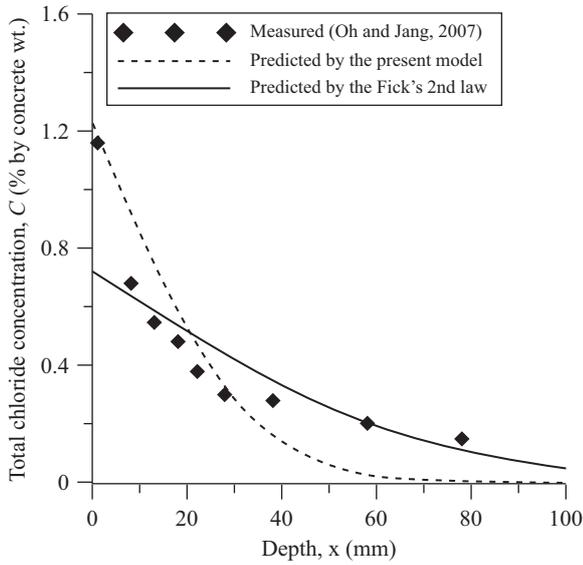
Fig. 3. Comparison of predicted and measured chloride profiles for specimens with w/c = 0.5 in field (tidal) conditions.

(a) Tidal conditions

(b) Submerged conditions

Fig. 4. Comparison of predicted chloride profiles for various chloride binding ratios.

structures as shown in the tests results worked by Oh and Jang (2007).

2. Effect of Exposure Condition

In such measure as the field (tidal) conditions, the predicted and measured chloride profiles are compared as indicated in the Fig. 3. It reveals that the chloride profile predicted by the proposed model is close to that of measured profile. The shape of this type of chloride profile follows as a consequence of the accumulation of chloride near the concrete surface, which is simulated by convection phenomenon considered by the proposed model and exposure condition. It is needed to point out that the field exposure conditions for tidal zone were idealized as sinusoidal change of the environmental conditions by Oh and Jang (2007). Fig. 3 shows that the chloride penetration into concrete can be fairly predicted for the tidal zone using this exposure condition. Fig. 3 also shows that the convection due to moisture transport can accelerate the chloride penetration into concrete and can cause the accumulation of chloride near the concrete surface. Fig. 3 again indicates that the prediction easily by Fick's second law is of large derivation from the test data done by Oh and Jang (2007). Accordingly, as a means to predict chloride penetration more exactly, the convection term should be considered practically in the theoretical formulation.

3. Effect of Chloride Binding

The chloride binding ratio has a numerous influence upon chloride penetration as indicated in Fig. 4. The higher the chloride binding ratio increases, the less the penetration of chloride ions into concrete becomes, and the less chloride content is accumulated in concrete. It is worthy to point out that the chloride binding ratio straight acts upon not only the overall
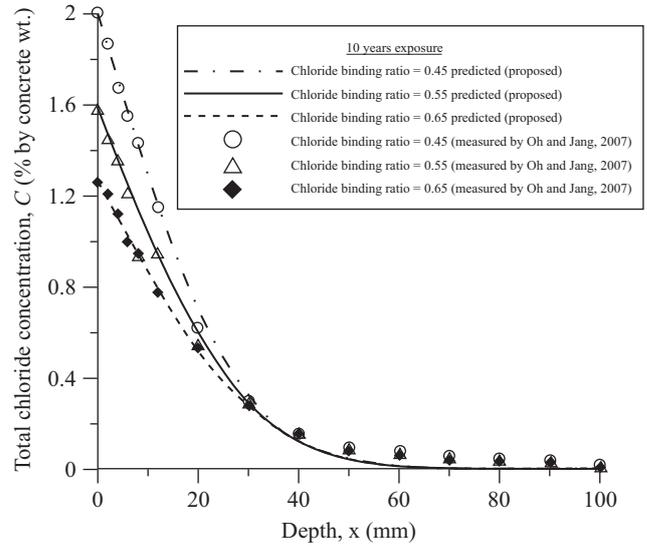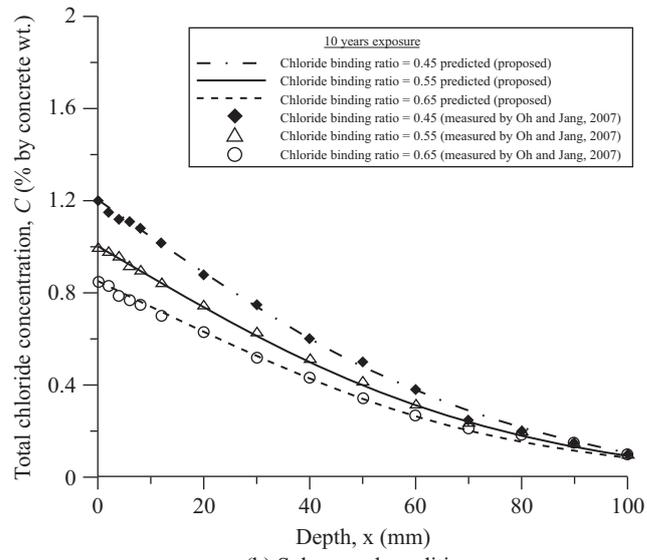
chloride profiles, but also the chloride content near the concrete surface. This is owing to the effect of chloride binding in concrete. This effect is reflected and quantitatively calculated in the proposed model. Fig. 4 illustrates that the chloride profile under tidal condition is found to be very much different from that under submerged condition. The present study result demonstrates that the different exposure conditions make over very much different profiles of chloride penetration. As a result, the effect of chloride binding has to be considered realistically in the analysis of chloride diffusion in concrete for real structures.

4. Effect of Time-Dependence

Fig. 5 illustrates the effect of time-dependence of diffusion

(a) Tidal conditions

(b) Submerged conditions
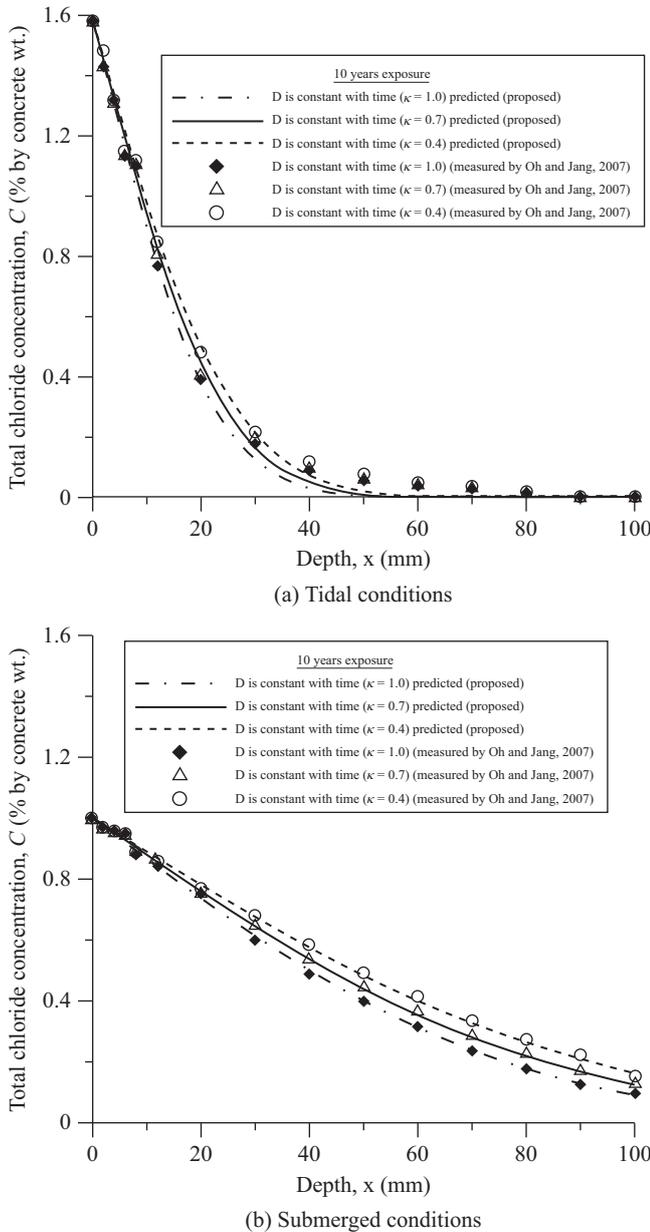
Fig. 5. **Comparison of predicted chloride profiles with time-dependence of diffusion coefficients.**

coefficient. The chloride penetration decreases when the time-dependence ratio (κ) increases. It is needed to point out that the diffusion coefficients used in the analysis are those values that are decided from the measured data of 10-year old field concrete worked by Oh and Jang (2007). The apparent diffusion coefficients (D_{ca}) before the test time are larger than those listed in Table 2 measured by Oh and Jang (2007) when the time-dependence ratio (κ) is less than unity. Accordingly, the effect of time-dependence of diffusion coefficient indicates that the penetrated chlorides become larger as κ value decreases as depicted in Fig. 5.

5. Effect of Temperature
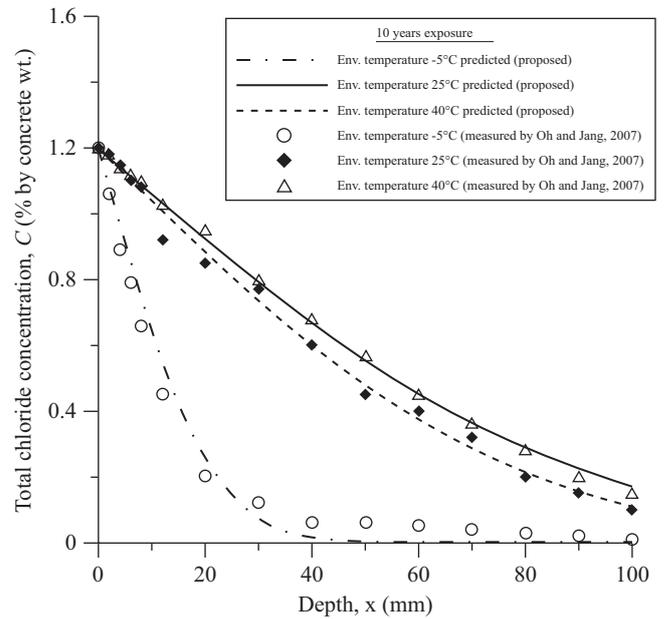
Fig. 6. **Comparison of predicted chloride profiles according to various temperature in concrete.**

Fig. 6 demonstrates the chloride ion penetration profiles in accordance with temperature -5, 25 and 40°C in concrete after 10-year exposure. In the case of the proposed model, the increase of temperature does increase largely the chloride penetration in concrete.

6. Effect of Relative Humidity

The relative humidity may also largely influence the penetration of chloride ions into concrete structures. Fig. 7 illustrates that the amount of chlorides penetrated into concrete increases as the relative humidity of concrete increases. This reason is that the chloride ions can move dissolved in pose water within concrete.

IV. CONCLUSIONS

The penetration of chloride into concrete was suggested by Oh and Jang (2007) to model considering the chloride diffusion by concentration gradient and chloride convection by moisture transport. Following this model, an analytical solution has been proposed by assumption that both the intrinsic diffusion coefficient and the mean velocity of moisture transport in concrete are time/depth dependence. The predicted results of the proposed model were studied and compared to the measured data in the laboratory and field tests worked by Oh and Jang (2007). Based on the studied results mentioned above, some valuable conclusions may be drawn as follows:

1. It is very clear that the diffusion coefficients of Type V cement mixtures are ordinarily larger than those of Type I cement mixtures. This is likely caused by the different binding effects of different types of cement. The C_3A
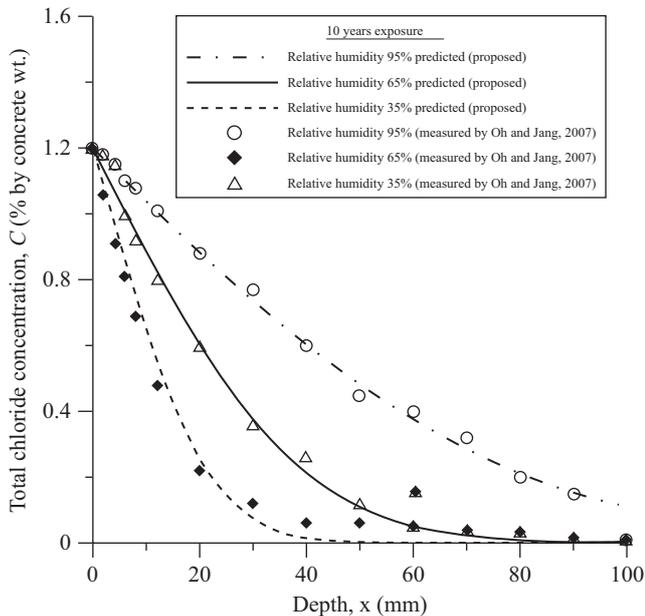
Fig. 7. Comparison of predicted chloride profiles according to various relative humidity in submerged conditions.

contents regularly affect the binding capacity. The C_3A content of Type V cement is smaller than that of Type I cement. It is also evidently seen that the replacement of fly ash into concrete diminishes the diffusion coefficients about 15-50%. This results in the less penetration depth of chloride ions into concrete structures.

2. The present study results reveal that the convection due to moisture transport can accelerate the chloride penetration into concrete and can cause the accumulation of chloride near the concrete surface. The predicted results obtained from the proposed method are compared with the field test data (Oh and Jang, 2007) for real concrete structures under tidal condition denotes that the prediction easily by Fick's second law of linear diffusion has large deviation from the test data, whereas the proposed method is in good agreement with really measured data worked by Oh and Jang (2007). As a result, for the purpose of predicting chloride penetration much more exactly, the convection term must be considered practically in the theoretical formulation.

3. The present study designates that the chloride binding ratio is of an important effect on chloride penetration. The higher the chloride binding ratio increases, the less the penetration of chloride ions into concrete becomes, and the less chloride content is cumulated in concrete. The result is contemplated and quantitatively enumerated in the proposed method.

4. The present study result illustrates that the different exposure conditions make over very much different profiles of chloride penetration. The chloride profile below tidal condition is discovered to be very much different from that below submerged condition. Accordingly, the effect of chloride must be considered realistically in the analysis of

chloride diffusion in concrete for real structures.

5. The chloride penetration decreases as the time-dependence ratio increases. As a result, the effect of time-dependence of diffusion coefficient shows that the penetrated chlorides become larger as the value of time-dependence ratio decreases.

6. The increase of temperature can increase largely the chloride penetration in concrete. This is due to that the intrinsic chloride diffusion coefficient is to be considered as a time/depth dependence in the proposed model. This is a remarkable phenomenon, because the higher temperature generally causes the higher penetration of chlorides.

7. The higher relative humidity may also causes larger accumulation of chloride in concrete. This is due to that the chloride ions can move dissolved in pore water within concrete.

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