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Effects of material and environmental parameters on chloride penetration profiles in concrete structures

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Abstract

On the basis of the transport mechanism of chloride ion, a prediction model of chloride penetration into concrete structures has been developed. The model includes the diffusion of chloride and its dependences on temperature, age, relative humidity, chloride binding and chloride convection by moisture transport. The experimental program has been set up to verify the model developed in the present study. Several series of concrete specimens were immersed in 3.5% chloride solutions for 15 weeks, and the chloride profiles of the specimens were measured and compared to the predicted chloride profiles. In addition, field measurements have been also conducted. From 10-year-old bridge piers, the chloride profiles in concrete under tidal zone were measured and compared with the predicted chloride profiles. The effects of chloride binding, relative humidity, temperature, exposure condition, and age-dependence on the chloride penetration in concrete were clarified from the present analyses. It was found from the present study that all these variables affect greatly the chloride penetration profiles in concrete. The comparison of the laboratory and field test data with the present theory confirms that the proposed model can be realistically used to predict the penetration of chloride ions into concrete structures under sea environments. Further, these results may be efficiently used for the realistic assessment and design for durability of concrete structures.

Keywords: Chloride diffusion; Concrete; Convection; Moisture transport; Chloride binding; Relative humidity; Age-dependence

1. Introduction

Recently, large-scale concrete structures such as nuclear power plants and offshore structures are actively being built in aggressive environment in many countries. Most of these structures are usually subject to chloride attack due to seawater or de-icing salt. Chloride-induced corrosion is one of the major causes of deterioration of such concrete structures [1–3]. Therefore, the resistance to chloride penetration becomes more important in the design and construction of concrete structures [1]. In general, Fick's 2nd law is a good approximation of the chloride penetration into concrete [4,5].

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (1)$$

By assuming $C(x,0)=0$, $C(0,t)=C_s$ and constant diffusion coefficient (D), the solution of Eq. (1) for semi-infinite concrete is

$$C(x,t) = C_s\left[1-erf\left(\frac{x}{\sqrt{4D_{ca}t}}\right)\right] \qquad (2)$$

The apparent diffusion coefficient, D_{ca}, is calculated from the concentration profiles of the cores taken from existing structures or the specimens tested in the laboratory by curve-fitting of Eq. (2), and D_{ca} values so calculated are used to predict the chloride penetration during longer periods [6]. Although this procedure is widely used, the chloride penetration into concrete is a more complex phenomenon for several reasons [7–9]: first, the diffusion coefficient is not constant parameters, but varies with age, temperature and relative humidity. Second, the chloride binding has a significant influence on chloride penetration because only free chloride can diffuse into bulk concrete. Third, not only chloride diffusion but also convection flow of chloride ions has an

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important role in moving the chloride ions in concrete, especially when exposed to drying–wetting condition. The boundary conditions are also more complicated to simulate the real exposure conditions.

The purpose of this paper is, therefore, first to explore the penetration mechanism of chloride ion, and to investigate the effects of various material and environmental parameters on the chloride penetration characteristics in concrete structures. On the basis of the transport mechanism, the prediction model of chloride penetration into concrete structures has been developed. The model includes the effects of several important factors such as

- chloride diffusion and its dependences on age, temperature and relative humidity
- chloride binding, and
- chloride convection by moisture transport.

An experimental program has been set up to verify the model developed in the present study. Several concrete specimens were immersed in 3.5% chloride solutions for 15 weeks, and the chloride profiles of the specimens were measured and compared to the predicted chloride profiles. In addition, field measurements also have been carried out. From a 10-year-old bridge, the chloride profiles of the tidal zone were measured and compared to the predicted profiles.

2. Model description

2.1. Chloride transport and binding

By the equation of mass balance [4], the one-dimensional chloride transport in concrete can be described as

$$\frac{\partial C}{\partial t}+\frac{\partial J_c}{\partial x}=0 \tag{3}$$

where C is the total chloride content in unit weight of concrete [kg/kg], and J_c is the chloride flux [m/s]. Considering the convection by moisture transport, the chloride flux can be written as follow [4].

$$J_c=-D_c\frac{\partial C_f}{\partial x}+\bar{u}C_f \tag{4}$$

where D_c is the intrinsic chloride diffusion coefficient[m^2/s], C_f is the free chloride content in unit weight of concrete [kg/kg], and $\bar{u}$ is the mean velocity of moisture transport in concrete[m/s]. Now, Eqs. (3) and (4) are rewritten as

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(D_c\frac{\partial C_f}{\partial x}\right)-\frac{\partial(\bar{u}C_f)}{\partial x} \tag{5}$$

Base on Freundlich isotherm [10], the chloride binding can be expressed as

$$C_b=\alpha C_f^{\beta} \tag{6}$$

where C_b is the bound chloride content in unit weight of concrete[kg/kg], and the parameters α and β are the empirical constants. In general, β is in the range of $0<\beta\leq 1$. If $\beta=1$, Eq. (6) represents the linear chloride binding, and represents the nonlinear chloride binding for $0<\beta<1$. While some experimental evidences show the nonlinearity of chloride binding [11], Sandberg [12] has reported that the relationship between free and total chlorides measured in field-exposed concrete is more linear compared to the corresponding relationship measured in the laboratory equilibrium experiments. So, for the sake of simplicity, the linear binding isotherm is assumed in the present model, i.e., $\beta=1$.

The total chloride content is the sum of free and bound chlorides, thus

$$C=C_f+C_b=C_f+\alpha C_f^{\beta} \tag{7}$$

For $\beta=1$,

$$C=C_f+\alpha C_b=(1+\alpha)C_f=\gamma C_f \tag{8}$$

where the binding capacity, $1/\gamma$ [$=1/(1+\alpha)$], is assumed to be constant. Substituting Eq. (8) into Eq. (5), the governing equation for total chloride transport becomes

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(\frac{D_c}{\gamma}\frac{\partial C}{\partial x}\right)-\frac{1}{\gamma}\frac{\partial(\bar{u}C)}{\partial x} \tag{9}$$

2.2. Moisture transport

The moisture mass balance equation without sink or source term (e.g., self-desiccation) becomes

$$\frac{\partial\theta}{\partial t}+\frac{\partial J_\theta}{\partial x}=0 \tag{10}$$

where θ is the moisture content in unit weight of concrete[kg/kg], and J_θ is the moisture flux[m/s] due to capillary suction and moisture diffusion. The moisture flux, J_θ, is given as [1]

$$J_\theta=\theta\bar{u}=-D_\theta\frac{\partial\theta}{\partial x} \tag{11}$$

where D_θ is the moisture diffusion coefficient [m^2/s]. Then, Eq. (11) becomes

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

From Eq. (11), the mean velocity of moisture flow is given as

$$\bar{u}=-\frac{D_\theta}{\theta}\frac{\partial\theta}{\partial x} \tag{13}$$

2.3. Diffusivity of concrete

The previous researches [13–16] have shown that the chloride diffusivity is a function of many factors, such as porosity, degree of hydration, aggregate size, temperature, humidity and local chloride concentration. In the present model, the dependences of the chloride diffusion coefficient were modelled by the following equations according to [8].

$$D_c=D_c^R f_T(T)\cdot f_t(t)\cdot f_h(h) \tag{14}$$

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 representing the dependences of D_c on temperature(T), age(t) and

Table 1
Mixture proportions for various test series

Specimen	Type of cement	Mixture proportions (kg/m^3)				
		Cement	Fly ash	Water	Sand	Gravel
C1	Type I	449	0	171	616	1050
C1FA20	Type I	359	90	171	616	1050
C5FA10	Type V	404	45	171	616	1050
C5FA20	Type V	359	90	171	616	1050

Note: Maximum aggregate size=20 mm.

pore relative humidity(h), which can be defined, respectively, by Eqs. (15), (16) and (17) [7,17].

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

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)].

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

where κ is the coefficient defined as the ratio between the diffusion coefficient for $t \rightarrow \infty$ and the diffusion coefficient for $t = t_0$(reference time), which varies from 0 to 1 according to Saetta et al. [8].

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

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) [16]. Here, based on the sorption and desorption isotherm [17,18], the pore relative humidity is simplified as

$$h = \frac{\theta}{\theta_{sat}} \tag{18}$$

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

2.4. Exposure conditions

The boundary conditions for prescribed flux can be expressed as

$$J_c^s = k_c(C_0 - C_f^s) + \bar{u}C_0 \tag{19}$$

$$J_\theta^s = k_\theta(\theta_0 - \theta^s) \tag{20}$$

where J_c^s and J_θ^s are the surface fluxes of chloride and moisture [m/s]. C_f^s and θ^s are the free chloride content and the moisture content at the surface, respectively. k_c and k_θ are the surface transfer coefficients of chloride and moisture[m/s]. C_0 and θ_0 account for the exposure environmental concentrations of chloride and moisture, which have the same units with C_f^s and θ^s. However, because the environmental chloride concentrations cannot be measured by weight of concrete, C_0 should be defined as

$$C_0 = \frac{\theta^s}{\rho_{sol}}\hat{C}_0 \tag{21}$$

where ρ_{sol} is the density of the pore solution[kg/m^3], and $\hat{C}_0$ is the measured chloride concentration [kg/m^3 of solution]. According to Eq. (18), θ_0 is also defined as

$$\theta_0 = \theta_{sat}h_0 \tag{22}$$

where h_0 is the environmental relative humidity.

3. Experimental program

3.1. Test variables

In order to verify the developed model, four series of test specimens were prepared. The major variables in the mixture proportions were the cement type and the addition of fly ash. The Type I (ordinary Portland cement) and Type V (sulphate resisting cement) were used and the contents of fly ash in the mixture were 10 and 20% of total cementitious materials, respectively. This was to see the effects of cement type and fly ash addition on the chloride diffusivity of concrete. The mixture proportions of the specimens are shown in Table 1.

3.2. Test method

40 concrete specimens ($\phi 10 \times 20$ cm) were continuously immersed in 3.5% chloride solutions for 15 weeks after 28-days water curing at 23 °C. All surfaces of the concrete specimens except top and bottom sides were sealed by epoxy resin so that the chloride penetration can occur only in one-direction. The solution was replenished every week to maintain uniform concentration, even though the reservoir is large enough. After immersion period, the total (acid-soluble) chloride profiles were measured.

3.3. Field measurements

The field measurements have been also carried out for 10-year-old bridge piers located in the estuary in Korea. Although the detailed mixture proportions of cores taken from the bridge are not known in advance, it was found from tests that the ordinary Portland cement was used, and the water-to-cement ratio is about 0.5, and the cement content is 350 kg/m^3. The total (acid-soluble) chloride profiles in the tidal zone (which is exposed to cyclic wetting and drying with 1-day cycle) were measured. Both laboratory and field measurement were

Table 2
Diffusion coefficients determined from the present tests

Apparent diffusion coefficients, D_{ca} ($\times 10^{-12}$ m^2/s)				
C1	C1FA20	C5	C5FA20	Field test
6.44	5.66	9.92	6.14	4.37

Table 3
Diffusion coefficients by other researchers [14,23]

D_{ca} ($\times 10^{-12}$ m^2/s) (W/B=0.6)		
OPC	OPC+30%FA	OPC+30%BFS
~20	3	5.5

Note: OPC = Ordinary Portland Cement.
FA = Fly Ash; BFS = Blast Furnace Slag.

performed by the titration procedures described in AASHTO T 260-84 [19], and two samples per each location were tested.

4. Results and discussion

The numerical solutions for laboratory and field conditions have been obtained by Petrov–Galerkin method [20,21] using finite elements. The continuously submerged laboratory conditions were modelled by setting environmental chloride concentration constant for the entire test period, and the field exposure conditions for tidal zone were expressed as sinusoidal change of environmental chloride concentrations with 1-day period (T), i.e.,

$$\hat{C}_0 = \frac{\hat{C}_0^{\max} - \hat{C}_0^{\min}}{2} \sin\left(\frac{2\pi t}{T}\right) + \frac{\hat{C}_0^{\max} + \hat{C}_0^{\min}}{2} \tag{23}$$

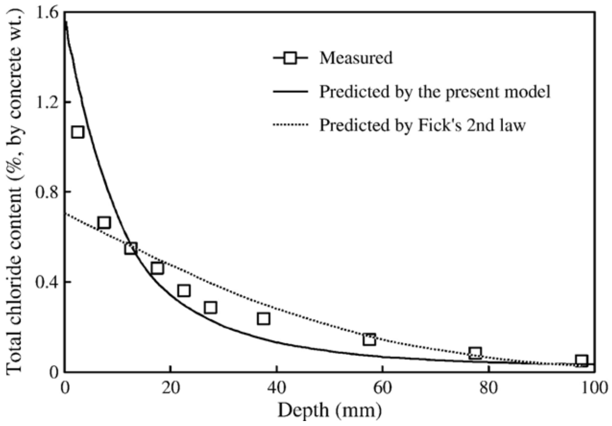


Fig. 2. Comparison of predicted and measured chloride profiles for specimens in field (tidal) conditions.

The apparent diffusion coefficients, D_{ca}, were determined by curve-fitting of Eq. (2) from measured data (Table 2), and the intrinsic diffusion coefficients are calculated by multiplying the binding capacity $1/\gamma$, which is assumed to be 0.55 based on the literature data [22,23]. The other parameters were assumed to be same for all specimens.

4.1. Effect of cement type

The result of Table 2 shows that the apparent diffusion coefficients of the series using Type I cement are smaller than those of the series using Type V cement. Table 2 also indicates

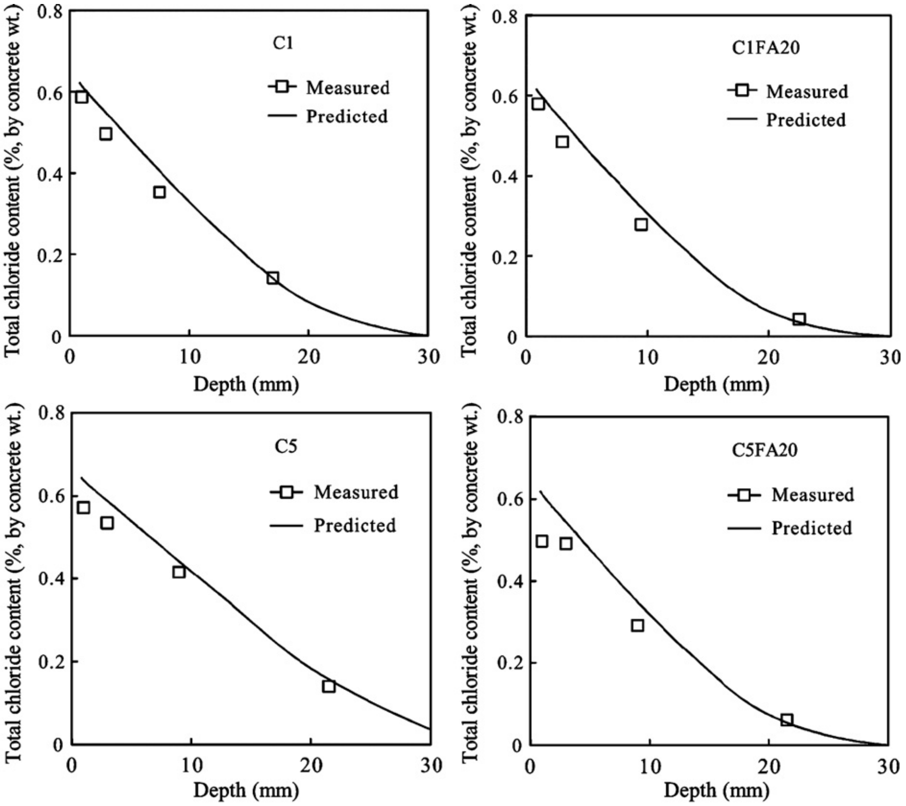


Fig. 1. Comparison of predicted and measured chloride profiles for specimens in laboratory conditions.

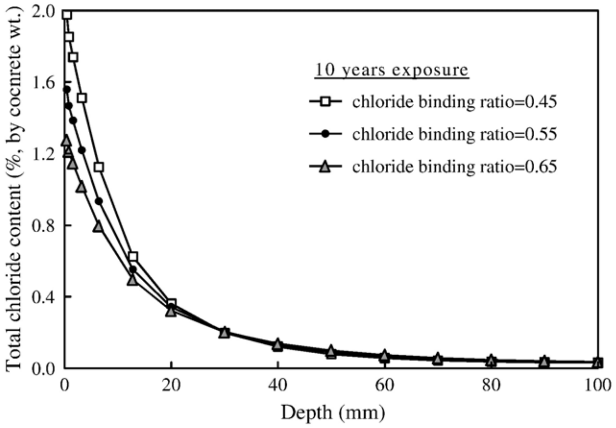
that the addition of fly ash reduces the diffusion coefficient and improves the resistance of concrete to chloride penetration. The values of chloride diffusivity by other researchers [15,24] are compared in Table 3.

The predicted chloride profiles for the laboratory test specimens are illustrated in Fig. 1. Fig. 1 shows that the predicted values correlate reasonably well with test data for chloride penetration.

4.2. Effect of exposure condition

For the tidal conditions, the predicted and measured chloride profiles are compared and shown in Fig. 2. Fig. 2 shows that the chloride profiles predicted by the present model are in good agreement with measurement, and the shape of chloride profiles is close to that of measured profiles. This type of chloride profile results from the accumulation of chloride near the concrete surface, which is simulated by convection phenomenon included in the present model and exposure condition. Although the sinusoidal change of the environmental conditions is ideal, the comparison of present model with test data indicates that the chloride penetration can be reasonably predicted for the tidal zone by using this exposure condition.

(a) Tidal conditions



(b) Submerged conditions

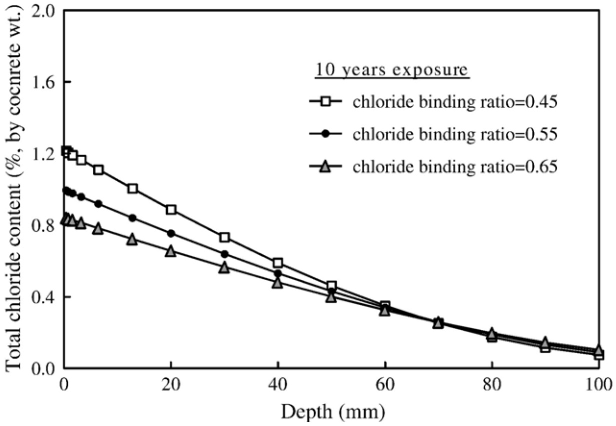
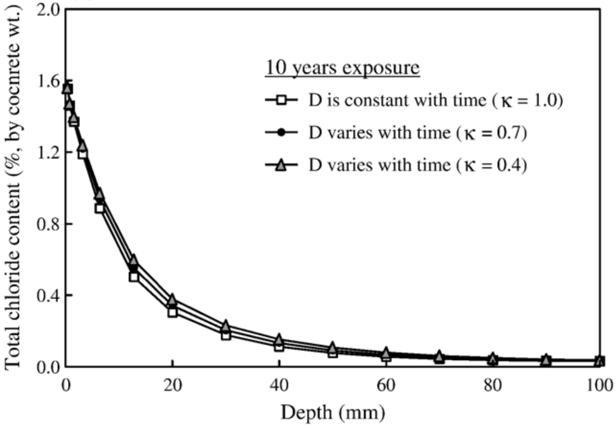


Fig. 3. Comparison of predicted chloride profiles for various chloride binding ratios.

(a) Tidal conditions



(b) Submerged conditions

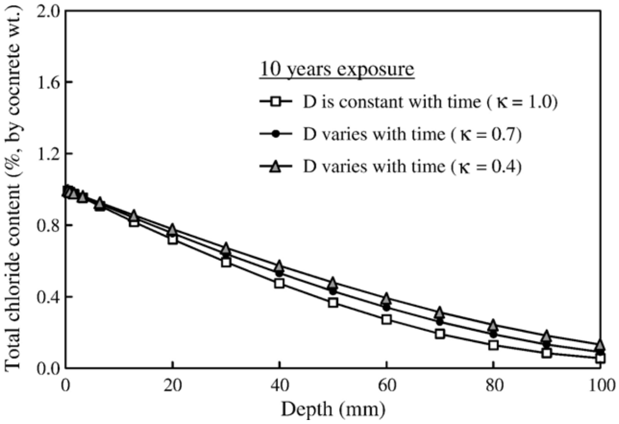


Fig. 4. Comparison of predicted chloride profiles with time-dependence of diffusion coefficients.

4.3. Effect of chloride binding

As shown in Fig. 3, the chloride binding ratio has a great influence on chloride penetration. The higher the chloride binding ratio becomes, the less chloride content is accumulated in concrete. It is interesting to note that the chloride binding ratio directly

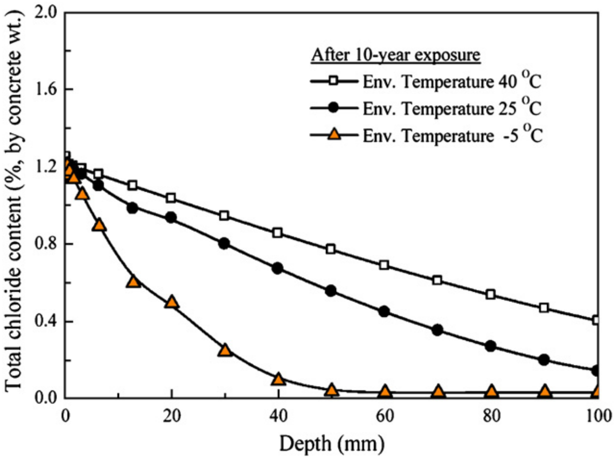


Fig. 5. Comparison of predicted chloride profiles according to various

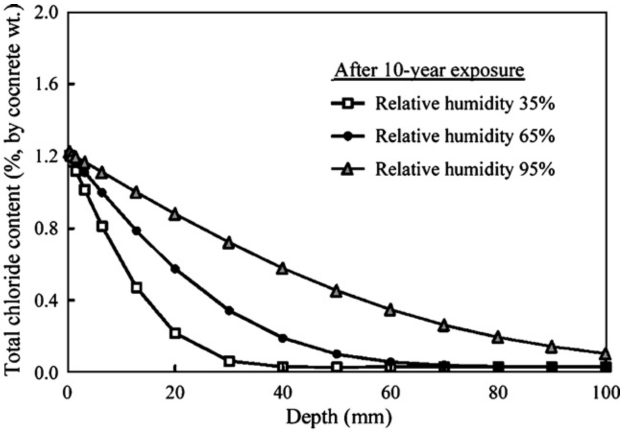


Fig. 6. Comparison of predicted chloride profiles according to various relative humidity in submerged conditions.

affects not only the overall chloride profiles, but also the chloride contents very near the concrete surface. This is due to the binding effect of chloride in concrete.

4.4. Effect of time-dependence

The effect of time-dependence of diffusion coefficient is demonstrated in Fig. 4. With an increase of time-dependence ratio (κ), the penetration of chloride decreases because the diffusion coefficients used in the analysis are those values that are determined from the measured data of 10-year old field concrete. That is, if the time-dependence ratio (κ) is less than unity, the diffusion coefficients before the test time are larger than those in Table 2. Therefore, in this case, the penetrated chlorides become larger as κ value decreases as shown in Fig. 4. The definition of time-dependence ratio κ is described in Eq. (16) in Section 2.3.

4.5. Effect of temperature

Fig. 5 shows the chloride ion penetration profiles according to various temperatures in concrete. From the figure, it can be said that the increase of temperature increases greatly the chloride penetration in concrete.

4.6. Effect of relative humidity

The relative humidity may also greatly affect the penetration of chloride ions into concrete structures. The amount of chlorides penetrated into concrete increases as the relative humidity of concrete increases as shown in Fig. 6. This is because the chloride ions can move dissolved in pore water.

5. Conclusions

The penetration of chloride into concrete has been modelled considering the chloride diffusion and its dependences on temperature, age, relative humidity, chloride binding and chloride convection by moisture transport. The numerical solutions of the proposed model for two different exposure conditions, submerged and tidal conditions, were investigated and compared to the measured data in the laboratory and field tests. From the results, the following conclusions were drawn.

1. The numerical investigations illustrate that the convection by moisture transport can accelerate the chloride ingress into concrete, and can bring about the accumulation of chloride near the concrete surface. Therefore, in order to predict chloride penetration more accurately, the convection term should be considered realistically in the formulation.
2. The present test results indicate that the addition of fly ash into concrete reduces the diffusion coefficients about 15–50%. This leads to less penetration of chloride ions into concrete structures shown in the present tests results.
3. It is seen that the diffusion coefficients of Type I cement mixtures are generally smaller than those of Type V cement mixtures. This is possibly due to the different binding effects of different types of cement. The C_3A contents usually affect the binding capacity and the C_3A content of Type I cement is higher than Type V cement.
4. The comparison of the theories with field test data for actual structures under tidal condition indicates that the prediction simply by Fick's 2nd law shows large deviation from the test data, while the proposed model agrees well with actual measured data.
5. The present study indicates that the different exposure condition yields very different profile of chloride penetration. The chloride profile under tidal condition is found to be much different from that under submerged condition. Therefore, this effect must be considered realistically in the chloride diffusion analysis for actual structures.
6. With an increase of chloride binding ratio, the penetration of chloride ions into concrete decreases. This effect is reflected and quantitatively calculated in the proposed model.
7. The present study indicates that the effect of time (age) dependence of diffusion coefficient on the chloride diffusion is not so large for well-cured concrete. However, the relative humidity and temperature affect greatly the chloride penetration profiles in concrete. The higher temperature causes higher penetration of chlorides. The higher relative humidity also causes larger accumulation of chloride in concrete. This is because the chloride ions move dissolved in pore water.

The proposed model may be efficiently used to predict the chloride penetration of actual structures under sea environments, if the chloride diffusion coefficients and the chloride binding ratios according to the mixture characteristics are obtained from the material data.

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