

Realistic Assessment of Chloride Penetration for Concrete Structures in Nuclear Power Plants

Byung Hwan Oh¹⁾, Seung Yup Jang¹⁾, Sun Woo Kim¹⁾ and Jung Moon Seo²⁾

1) Dept. of Civil Engineering, Seoul National University, Seoul, Korea

2) Korea Atomic Energy Research Institute, Daejeon, Korea

ABSTRACT

On the basis of the transport mechanism of chloride ion, the prediction model of chloride penetration into concrete structures has been developed. The model includes the diffusion of chloride and its dependences on temperature, age and 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 also have been conducted. From a 10-year-old bridge, the chloride profiles of the tidal zone were measured and compared to the predicted chloride profiles. The comparison of the laboratory and field test results with theory confirms that the model developed in the present study can be realistically used to predict the penetration of chloride ions into concrete structures under sea environments.

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 seawater or de-icing salt. Chloride-induced corrosion is one of the major causes of deterioration of such concrete structures. Therefore, the resistance to chloride penetration becomes more important in the design and construction of concrete structures.

In general, Fick's 2nd law is a good approximation of the chloride penetration into concrete [1].

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

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

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

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 [2]. Although this procedure is widely used, the chloride penetration into concrete is more complex phenomenon for several reasons: 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 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 study is, therefore, to explore the penetration mechanism of chloride ion, and to establish the methods for predicting chloride penetration into concrete structures. On the basis of the transport mechanism, the prediction model of chloride penetration into concrete structures has been developed. The model developed in the present study is based on the model proposed by Bazant [3] and Saetta et al [4]. 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.

MODEL DESCRIPTION

Chloride Transport and Binding

By the equation of mass balance [1], the one-dimensional chloride transport in concrete can be described as

$$\frac{\partial C}{\partial t} + \frac{\partial J_c}{\partial x} = 0 \quad (3)$$

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 [1].

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

where D_c is the intrinsic chloride diffusion coefficient [m²/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, Eq.(3) and (4) are rewritten as

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

Base on Freundlich isotherm [6], the chloride binding can be expressed as

$$C_b = \alpha C_f^\beta \quad (6)$$

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 [7], Sandberg [8] 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

$$C = C_f + C_b = C_f + \alpha C_f^\beta \quad (7)$$

For $\beta=1$,

$$C = C_f + \alpha C_b = (1 + \alpha) C_f = \gamma C_f \quad (8)$$

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

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

Moisture Transport

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

$$\frac{\partial \theta}{\partial t} + \frac{\partial J_\theta}{\partial x} = 0 \quad (10)$$

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]

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

where D_θ is the moisture diffusion coefficient [m²/sec]. Then, Eq.(11) becomes

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

And then, from Eq.(12), the mean velocity of moisture flow is given as

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

Diffusivity of Concrete

The previous researches [9-11] 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 modeled by the following equations according to [4].

$$D_c = D_c^R f_T(T) \cdot f_i(t) \cdot f_h(h) \quad (14)$$

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 pore relative humidity(h), which can be defined, respectively, by Eq.(15), (16) and (17)[3,12].

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

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)].

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

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 [4].

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

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) [12]. Here, based on the sorption and desorption isotherm [13], the pore relative humidity is simplified as

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

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

Exposure Conditions

The boundary conditions for prescribed flux can be expressed as

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

$$J_\theta^s = k_\theta(\theta_0 - \theta^s) \quad (20)$$

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

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

where ρ_{sol} is the density of the pore solution[kg/m³], and \hat{C}_0 is the measured chloride concentration [kg/m³ of solution]. According to Eq.(18), θ_0 is also defined as

$$\theta_0 = \theta_{sat} h_0 \quad (22)$$

where h_0 is the environmental relative humidity.

Table 1. Mixture proportions

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

EXPERIMENTAL PROGRAM

In order to verify the developed model, 40 concrete specimens ($\phi 10 \times 20 \text{ cm}$) were continuously immersed in 3.5% chloride solutions for 15 weeks. 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. The mixture proportions of the specimens are shown in table 1.

The field measurements have been also carried out for a 10-year-old bridge located in the estuary. The total (acid-soluble) chloride profiles in the tidal zone were measured. Both laboratory and field measurement were performed by the titration procedures described in AASHTO T 260-84 [14].

RESULTS AND DISCUSSION

The numerical solutions for laboratory and field conditions have been obtained by Petrov-Galerkin method [15,16] using finite elements with identical material parameters. The continuously submerged laboratory conditions were modeled 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 one-day period (T), i.e.,

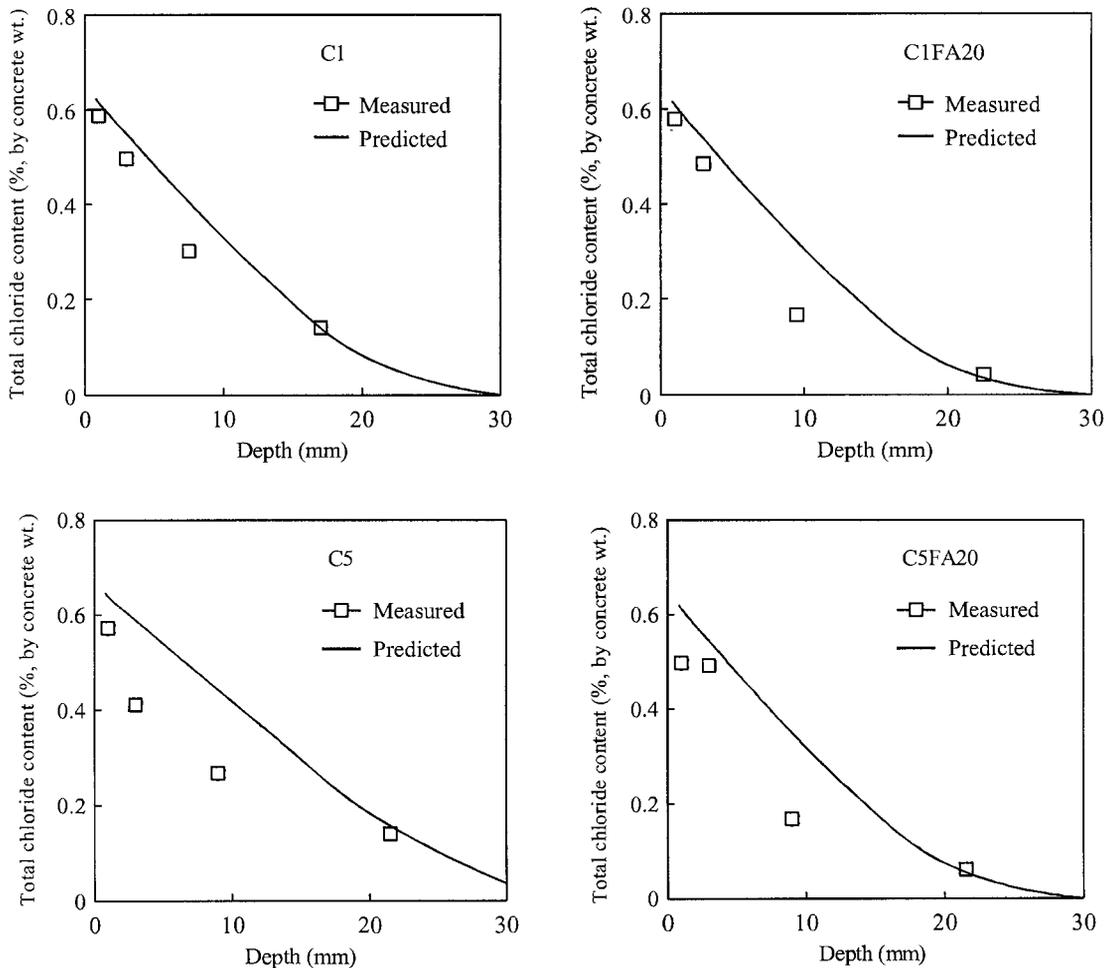


Fig. 1 Comparison of predicted and measured chloride profiles, laboratory conditions

Table 2. Apparent diffusion coefficients determined by curve-fit using Fick's 2nd law

	C1	C1FA20	C5	C5FA20	Field test
$D_{ca}(m^2/sec)$	6.44×10^{-12}	5.66×10^{-12}	9.92×10^{-12}	6.14×10^{-12}	4.37×10^{-12}

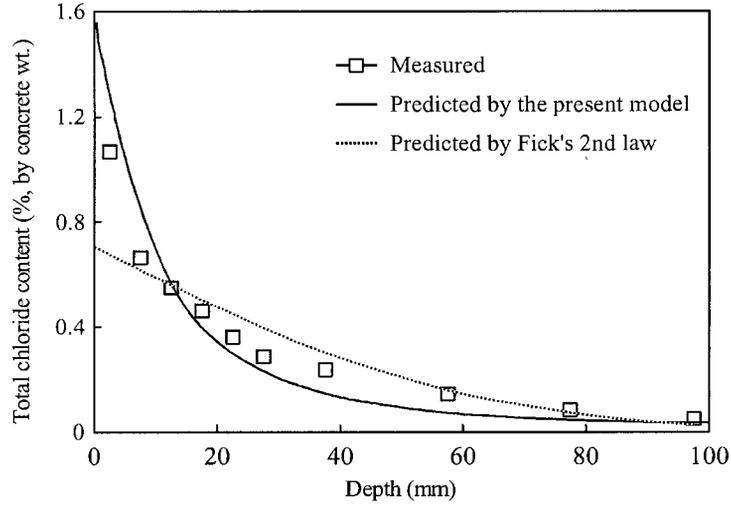


Fig. 2 Comparison of predicted and measured chloride profiles, field (tidal) conditions

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

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, γ (assumed to be 0.55 [17]). The other parameters were assumed to be same for all specimens.

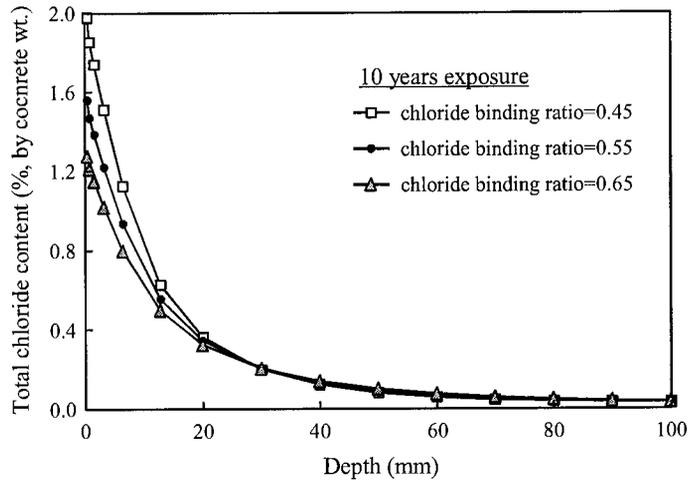
The results of Table 2 shows that the apparent diffusion coefficients of the series using Type I cement are smaller than those of the series using Type V cement, and the use of fly ash can improve the concrete resistance to chloride penetration. Especially, the combination of Type V and fly ash seems to be more effective to lower the chloride ingress than the combination of Type I cement and fly ash.

The predicted chloride profiles for the laboratory test specimens are illustrated in Fig. 1. As shown in Fig.1, the predicted chloride contents are larger than the measured data for all specimens. This is because the convection by moisture transport is included in the present model, which implies that the diffusion coefficients determined on the basis of Fick's 2nd law could be overestimated.

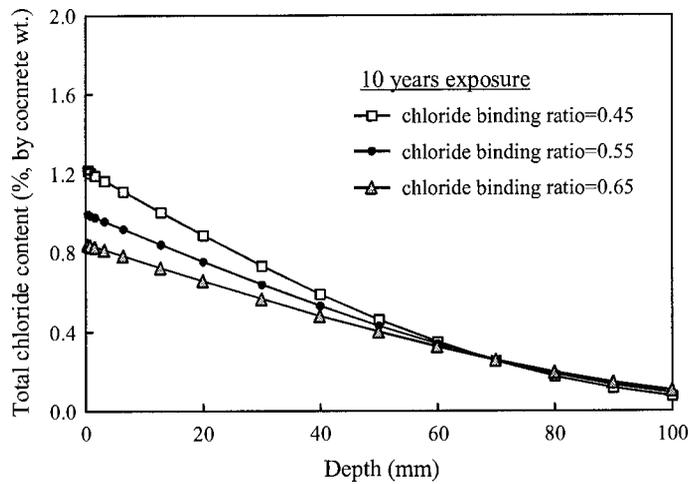
For the tidal conditions, the predicted and measured chloride profiles are compared (Fig. 2). Fig. 2 shows that the chloride profiles predicted by the present model are in good agreement with measurement, and the shape of chloride profiles is close to that of measured profiles. This type of chloride profiles result from the accumulation of chloride near the concrete surface, which is simulated by convection phenomenon included in the present model. Although the sinusoidal change of the environmental conditions is ideal, the chloride penetration can be more accurately predicted for the tidal zone from this type of exposure conditions if the material parameters can be more reasonably identified.

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. If the non-linearity of chloride binding is considered ($0 < \beta < 1$), the chloride profiles will be much more complicated [18].

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 that determined by curve-fitting of Eq.(2) from the measured data. That is, if the time-dependence ratio (κ) is not unity, the diffusion coefficients before the test time are larger than those in Table 2.



(a) Tidal conditions



(b) Submerged conditions

Fig. 3 Comparison of predicted chloride profiles with chloride-binding ratios

Fig. 5 shows that the chloride ion penetration profiles according to various temperature in actual climate ranges. It is seen that temperature does not seem to have a significant effect on chloride penetration in usual climate ranges. However, the relative humidity greatly affects the penetration of chloride ions into concrete structures, as shown in Fig. 6. The chloride content increases as the relative humidity of concrete increases. This is because the chloride ions can only move dissolved in pore water.

CONCLUSIONS

The penetration of chloride into concrete has been modeled considering the chloride diffusion and its dependences on temperature, age and 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.

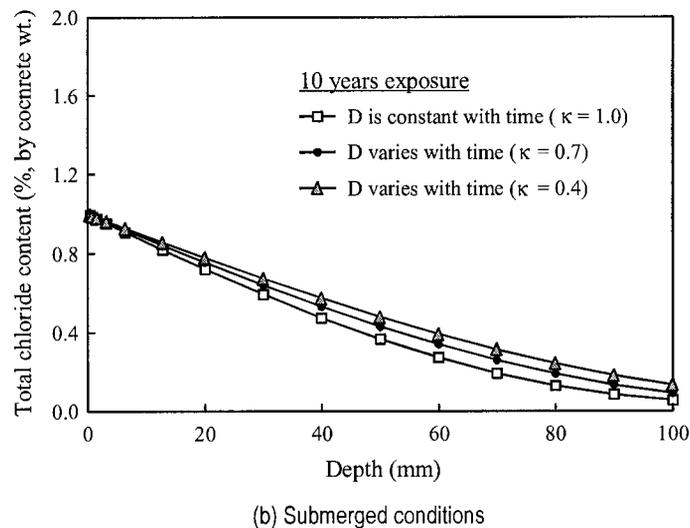
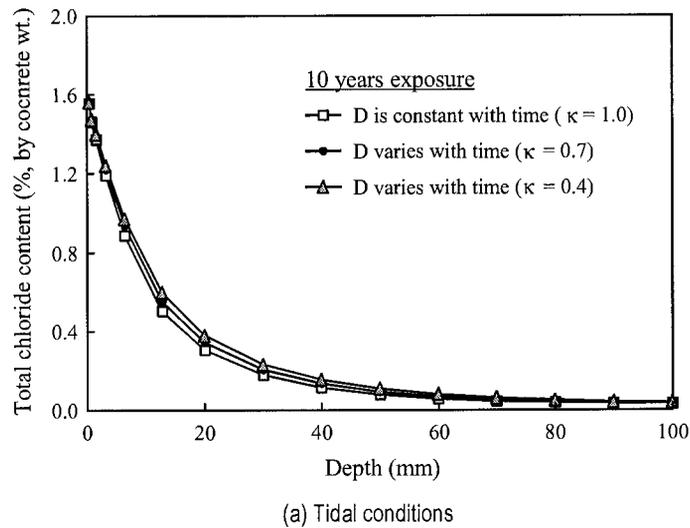


Fig. 4 Comparison of predicted chloride profiles with time-dependence of diffusion coefficients

- The present test results indicate that the addition of fly ash into concrete reduces the diffusion coefficients about 15~50 percent. This leads to less penetration of chloride ions into concrete structures shown in the present tests results.
- 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 comparison of the theories with field test data for actual structures under tidal condition indicates that the prediction by Fick's 2nd law shows large deviation from the test data, while the proposed model agrees well with actual measured data.
- With an increase of chloride-binding ratio, the penetration of chloride ions into concrete decreases. This effect is quantitatively calculated in the proposed model.
- The present study indicates that the effect of time (age) and temperature dependence of diffusion coefficient on the chloride diffusion is not large for small variation of diffusion coefficient. However, the relative humidity greatly affects the chloride penetration because the chloride ions can only move dissolved in pore water.
- The proposed model may be efficiently used to predict the chloride penetration of actual structures under sea environments.

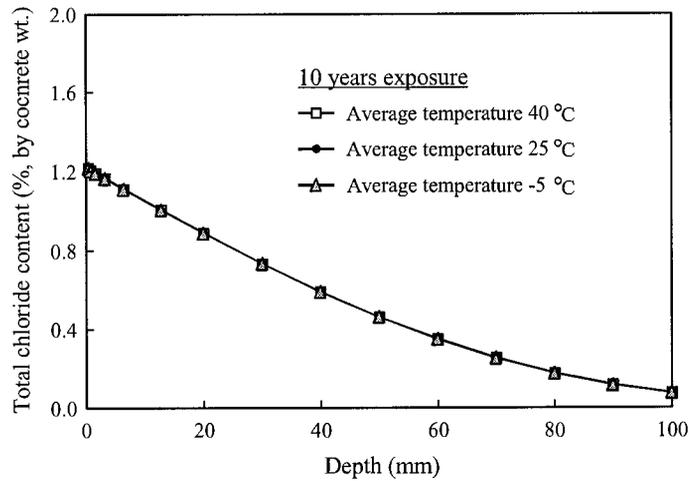


Fig. 5 Comparison of predicted chloride profiles according to temperature in submerged conditions

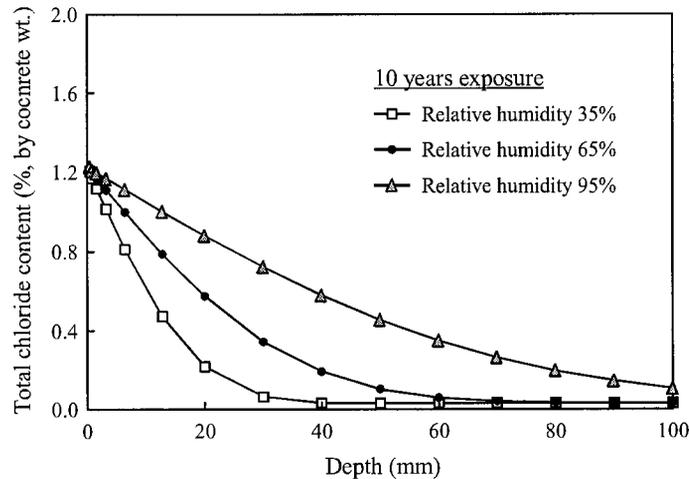


Fig. 6 Comparison of predicted chloride profiles according to relative humidity in submerged conditions

REFERENCES

1. Crank, J., *The Mathematics of Diffusion*, 2nd Ed, Oxford, Clarendon, 1975.
2. Tuutti, K., *Corrosion of Steel in Concrete*, CBI Report No.4-82, Swedish Cement and Concrete Research, Stockholm, Swenden, 1982.
3. Bazant, Z.P., "Physical model for steel corrosion in concrete sea structures-theory," *ASCE Journal of Structural Division*, Vol.105, No.6, 1979, pp.1137-1153.
4. Saetta, A. V., Scotta, R. V. and Viataliani, R. V., "Analysis of chloride diffusion into partially saturated concrete," *ACI Material Journal*, Vol.90, No.5, 1993, pp.441-451.
5. Balabanic, G., Bicanic, N. and Đurekovic, A., "Mathematical modeling of electro-chemical steel corrosion in concrete," *ASCE Journal of Engineering Mechanics*, Vol.122, No.12, 1996, pp.1113-1122.
6. Bear, J. and Buchlin, J.-M., *Theory and Applications of Transport in Porous Media, Vol.5: Modelling and Applications of Transport Phenomenon in Porous Media*, 1st Ed., Kluwer Academic Publishers, Dordrecht, 1991.
7. Tang, L. and Nilsson, L.-O., "Chloride binding capacity and binding isotherms of opc pastes and mortars," *Cement and*

- Concrete Research*, Vol.23, 1993, pp.247-253.
8. Sandberg, P., "Studies of chloride binding exposed in a marine environment," *Cement and Concrete Research*, Vol.29, 1999, pp.473-477.
 9. Kropp, J. and Hilsdorf, H.K. *Performance Criteria for Concrete Durability*, Rilem Repot 12, Rilem, Paris, 1995.
 10. Tang, L., "Electrically accelerated methods for determining chloride diffusivity in concrete – current development," *Magazine of Concrete Research*, Vol.48, No.176, 1996, pp.173-179.
 11. Mangat, P.S. and Molloy, B.T., "Prediction of long term chloride concentration in concrete," *Material and Structures*, Vol.27, 1994, pp.338-346.
 12. Bazant, Z.P. and Thonguthai, W., "Pore pressure and drying of concrete in high temperature," *ASCE Journal of the Engineering Mechanics*, Vol.104, No.5, 1978, pp.1059-1079.
 13. Bazant, Z.P. and Najjar, L.J., "Drying of concrete as a nonlinear diffusion problem," *Cement and Concrete Research*, Vol.1, 1971, pp.461-473.
 14. "Standard method for sampling and testing of total chloride ion in concrete and concrete raw materials," AASHTO Designation T 260, American Society of State Highway and Transportation Officials, Washington D.C.
 15. Bathe, K.J., *The Finite Element Procedures*, 1st Ed., Prentice Hall: Englewood Cliffs, New Jersey, 1996.
 16. Huyakorn, P.S. and Nikuha, K., "Solution of transient transport equation using an upstream finite element scheme," *Applied Mathematical Modelling*, Vol.3, 1979, pp.7-17.
 17. Arya, C. and Newman, J.B., "An Assessment of Four Methods of Determining the Free Chloride Content of Concrete," *Materials and Structures*, Vol.23, 1990, pp.319-330.
 18. Martín-Pérez, B., Zibara, H., Hooton, R.D. and Thomas, M.D.A., "A study of effect of chloride binding on service life predictions," *Cement and Concrete Research*, Vol.30, 2000, pp.1215-1223.