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Modeling of chloride ion ingress in coastal concrete

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Abstract

The behavior of chloride ions introduced into concrete from concrete surface by marine environment and by use of marine aggregate was analyzed for a coastal concrete structure. A mathematical model including the diffusion of chloride ion in aqueous phase of pores, the adsorption and desorption of chloride ions to and from the surface of solid phase of concrete, and the chemical reactions of chloride ions with solid phase was presented. Finite element method was employed to carry out numerical analysis. Quantitative analysis was conducted to measure the distribution of the free chloride ion concentration in aqueous phase of concrete with potentiometric titration based on ASTM D 1820. The concentration profiles of chloride ions predicted by the mathematical model agreed favorably with the measured data. The results of this study may be used to predict the onset of reinforcement corrosion and to identify the maximum limit of chloride ions contained in concrete admixtures. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Properly constituted, placed, and cured concrete has a long service life under most natural and industrial environments. However, premature failures of concrete structures may occur due to various physical and chemical effects [1,2]. Steel bars in reinforced concrete are protected from corrosion in the presence of moisture and oxygen by a microscopic oxide layer that forms on their surface due to the high alkalinity (pH 13) of the surrounding concrete. In the absence of chloride ions in aqueous phase of concrete pore, the protective film on steel is reported to be stable as long as the value of pH stays above 11.5 [3]. In the presence of chloride ions, it is reported that the protective film may be destroyed even at pH values considerably above 11.5, because the protective film becomes permeable and unstable, when the concentration of chloride ions in the pore water in the vicinity of the bars exceeds a threshold value, of the order of 0.05 wt. in concrete [4]. The transformation of metallic iron to rust is accompanied by an increase in volume that, depending on the state of oxidation, may be as large as 600% of the original metal. This volume increase is believed to be the principal cause of concrete expansion and cracking. The onset of cracks due to reinforcement corrosion enhances the intrusion of moisture, oxygen, and chloride ions and, therefore, accelerates the deterioration of concrete structure [5].

Recently, premature reinforcement corrosion in concrete structures exposed to chloride containing environments has created an important problem. This is due to an increase of concrete construction in marine environments and an increasing use of marine aggregate of chloride containing admixture at the mixing stage as well as the use of deicing agents in cold-weather area [6].

In this study, the behavior of chloride ions introduced into concrete from concrete surface by a marine environment and contained in admixture at the mixing stage was modeled. The physicochemical processes including the diffusion of chloride ion in aqueous phase of pores, the adsorption and desorption of chloride ions to and from the surface of solid phase of concrete, and the chemical reaction of chloride ion with solid phase were analyzed by using the finite element

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method. In order to validate the model, the calculated distributions of chloride ion concentration in concrete were compared with the measured data.

2. Model formulation

A schematic of the problem domain (i.e., the cross section of a corner of concrete structure) is shown in Fig. 1(a). The dimensions of the domain are shown in Fig. 1(b). The change of the chloride ion concentration is traced at three locations A, B, and C where steel bars are embedded.

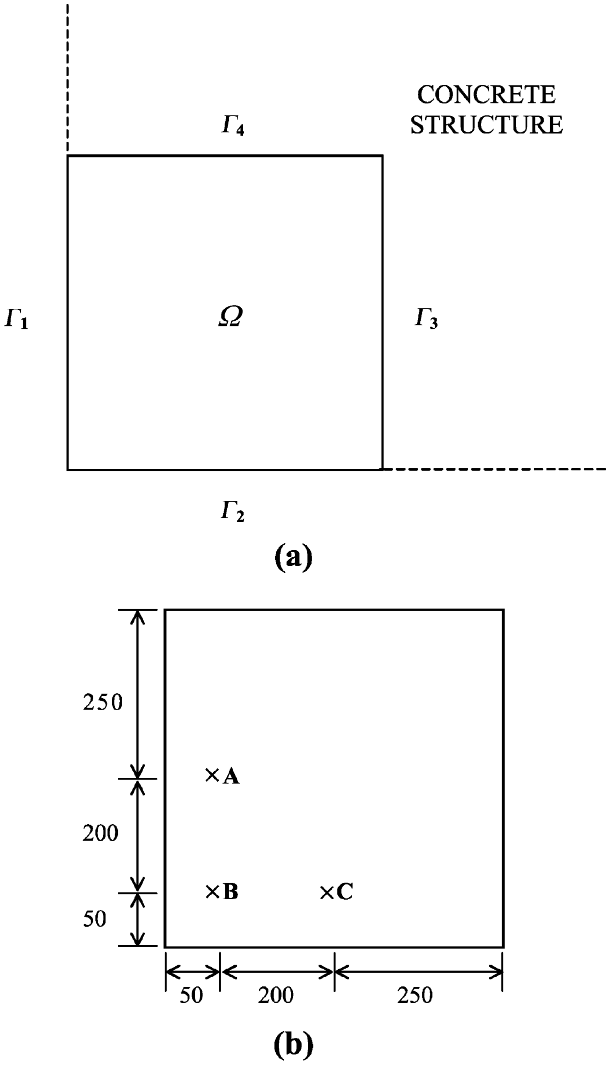


Fig. 1. (a) Problem domain and boundaries and (b) dimension of problem domain.

The chloride ions dissolved in pore water of concrete, $Cl^-(aq)$, are adsorbed by calcium silicate hydrate (C-S-H) and by the other constituents of hardened cement paste. They also chemically react with C_3A and C_4AF constituents of cement ($3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, respectively) and producing the so-called Friedel's salt. Some of the adsorbed chloride ion, $Cl^-(s)$, are desorbed and the process tends to equilibrium between $Cl^-(aq)$ and $Cl^-(s)$ [4]. Therefore, the net rate of binding Cl^- in the solid phase, r, is given by Eq. (1)

$$r = k_a \varepsilon f[Cl^-(aq)][Cl^-(s)]_{sat} - [Cl^-(s)] - \frac{k_a}{K_{eq}}[Cl^-(s)] \tag{1}$$

where k_a and K_{eq} are kinetic constant of a desorption and equilibrium constant, respectively, ε is the concrete porosity, f is the fraction of pore volume filled with water, and $Cl^-(aq)$ and $Cl^-(s)$ are the concentrations of Cl^- in aqueous and solid phases, respectively.

The mass balance equations of $Cl^-(aq)$ and $Cl^-(s)$ are expressed as in Ref. [4] (Eqs. (2) and (3)):

$$\frac{\partial(\varepsilon f[Cl^-(aq)])}{\partial t} = \nabla^2(D_{e,Cl^-}[Cl^-(aq)]) - r \text{ in } \Omega \tag{2}$$

$$\frac{\partial(\varepsilon f[Cl^-(s)])}{\partial t} = r \text{ in } \Omega \tag{3}$$

where D_{e,Cl^-} is the effective diffusivity of Cl^- in concrete, t is the time, and Ω is the problem domain shown in Fig. 1(a).

The boundary and initial conditions applied are

$$[Cl^-(aq)] = [Cl^-(aq)]_1 \text{ at } \Gamma_1 \tag{4}$$

$$[Cl^-(aq)] = [Cl^-(aq)]_2 \text{ at } \Gamma_2 \tag{5}$$

$$\frac{\partial[Cl^-(aq)]}{\partial n} = 0 \text{ at } \Gamma_3 \text{ and } \Gamma_4 \tag{6}$$

$$\frac{\partial[Cl^-(s)]}{\partial n} = 0 \text{ at } \Gamma_1, \Gamma_2, \Gamma_3, \text{ and } \Gamma_4 \tag{7}$$

$$[Cl^-(aq)] = [Cl^-(aq)]_{in} \text{ in } \Omega \quad \text{at } t = 0 \tag{8}$$

$$[Cl^-(s)] = [Cl^-(s)]_{in} \text{ in } \Omega \text{ at } t = 0. \tag{9}$$

Boundary conditions (4) and (5) imply that the concentrations of $Cl^-(aq)$ at Γ_1 and Γ_2 have fixed values, which are dependent on the external environment of concrete structure. Boundary condition (6) implies that $Cl^-(aq)$ does not penetrate to the normal direction of Γ_3 and Γ_4. Boundary condition (7) implies that $Cl^-(s)$ does not move through the boundaries. $[Cl^-(aq)]_{in}$ of Eq. (8) and $[Cl^-(s)]_{in}$ of Eq. (9)

denote the initial concentrations of Cl^- in aqueous and solid phases, respectively.

3. Finite element formulation

The functional spaces of Sobolev type employed as follows (Eqs. (10)–(12), see also Eq. (13)):

$$H^1(\Omega) = \left\{ W \mid W \in L^2(\Omega), \frac{\partial w}{\partial x} \in L^2(\Omega), \frac{\partial w}{\partial y} \in L^2(\Omega) \right\} \tag{10}$$

$$V(\Omega) = \{ W \mid W \in H^1(\Omega), W = 0 \text{ on } \Gamma_1 \text{ and } \Gamma_2 \} \tag{11}$$

$$S(\Omega) = \{ W \mid W \in H^1(\Omega), W = [\mathrm{Cl}^-(\mathrm{aq})]_1 \text{ on } \Gamma_1, \\ W = [\mathrm{Cl}^-(\mathrm{aq})]_1 \text{ on } \Gamma_2 \} \tag{12}$$

where

$$L^2(\Omega) = \left\{ w \mid \int_\Omega W^2 \mathrm{d}\Omega < +\infty \right\}. \tag{13}$$

The variational form of the problem can be stated as follows.

Find $\Phi^1 \in S$, $\Phi^2 \in H^1$ such that

$$\int_\Omega W^1 \left(\varepsilon f \frac{\partial \Phi^1}{\partial t} \right) \mathrm{d}\Omega + \int_\Omega \nabla W^1 \cdot (D_{\mathrm{e,Cl^-}} \nabla \Phi^1) \mathrm{d}\Omega \\ + \int_\Omega W^1 r \mathrm{d}\Omega = 0, \forall W^1 \in V \tag{14}$$

$$\int_\Omega W^2 \frac{\partial \Phi^2}{\partial t} \mathrm{d}\Omega + \int_\Omega W^2 r \mathrm{d}\Omega = 0, \forall W^2 \in H^1 \tag{15}$$

where r is a nonlinear function of Φ^1 and Φ^2.

A finite element spatial discretization of Eqs. (14) and (15) leads to a set of nonlinear ordinary differential equations (Eqs. (16) and (17)):

$$\mathbf{M}\boldsymbol{d} + \boldsymbol{N}(\dot{\boldsymbol{d}}) = \boldsymbol{F} \tag{16}$$

$$\boldsymbol{d}(0) = \boldsymbol{d}_0 \tag{17}$$

where $\boldsymbol{d}$ is the vector of nodal values of unknowns, $\dot{\boldsymbol{d}}$ is its time derivative, $\mathbf{M}$ is the mass matrix, $\boldsymbol{N}$ is the nonlinear vector function of $\boldsymbol{d}$. $\boldsymbol{F}$ is the right-hand side constant vector and $\boldsymbol{d}_0$ is a given vector corresponding to the initial conditions (8) and (9). These equations are solved by a predictor/multicorrector temporal integration scheme [7].

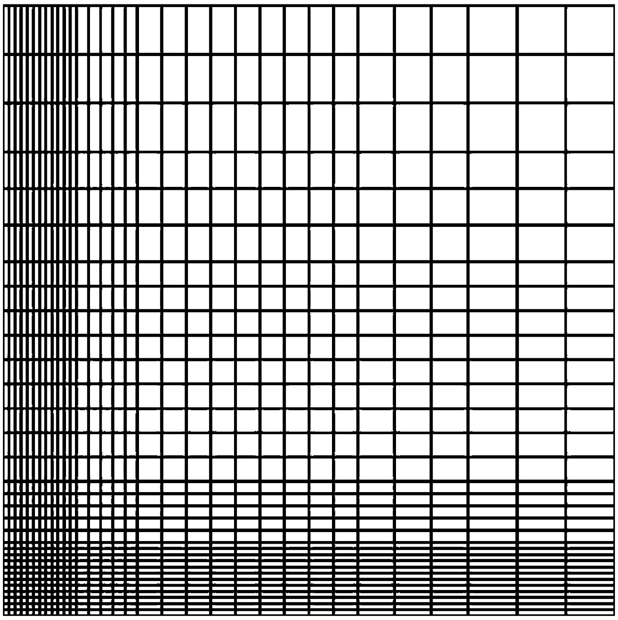


Fig. 2. Finite element mesh used.

The finite element mesh used is shown in Fig. 2. The element mesh was made denser around the walls where steeper concentration gradients are expected. A total of 1024 bilinear quadrilateral elements (and 1089 nodes) were used for the mesh. Calculations were performed on HP 715/50 workstation. The CPU time required for one time step was 3 s.

4. Results and discussions

In this study, the base values of $[\mathrm{Cl}^-(\mathrm{aq})]_1$ and $[\mathrm{Cl}^-(\mathrm{aq})]_2$ were fixed as 0.22 and 0.10 wt.% of concrete to investigate the effects of the surface concentration of chloride ions. The base values were used unless noted otherwise. As initial conditions, two cases with and without initial presence of Cl^- in the admixture were considered. The value of Cl^- was 0.3 wt.% for the case when chloride ion is introduced at the mixing stage by using marine aggregate. The values of the parameters used for the calculations were summarized in Table 1. The porosity, ε, was measured with mercury porosimetry by using Poresizer 9320 from Micrometrics Instrument. The fraction of pore volume filled with water, f, was set as 0.7. Upon our experiences of numerical simulations, the values of f working well for the analysis were 0.7 for the marine structure not immersed in water and 1.0 for the one that was immersed in water. The effective diffusivity of chloride ion in concrete, $D_{\mathrm{e,Cl^-}}$ was determined to obtain the

Table 1
Parameters used in calculations

Parameter	Value
ε	0.20
f	0.7
D_e	2.0×10^{-12} m^2/s
k_a	1×10^{-5} m^3/mol s
$[\mathrm{Cl}^-(\mathrm{s})]_{\mathrm{sat}}$	214 mol/m^3
K_{eq}	1.64×10^{-2} m^3/mol

best fit of the measured profiles of chloride ion concentration in concrete. The values used for the other parameters such as k_a, $[\mathrm{Cl}^-(\mathrm{s})]_{\mathrm{sat}}$, and K_{eq} were the ones used by Papadakis et al. [4] for the concrete, of which the water-to-cement and aggregate-to-cement ratios were 0.65 and 5.85, respectively. We did not conduct the quantitative analysis for the compositions of cement and concrete. However, a good agreement of the calculated results with the measured data that will be shown in Fig. 7 suggests that the compositions of cement and concrete considered in this study may be similar to those of Ref. [4].

Fig. 3 shows the variation of chloride ion concentrations of aqueous and solid phase with time for the case without initial presence of chloride ion at three locations A, B, and C where steel bars are embedded. In this case, there exist only external sources of chloride ion penetrating through the surface of concrete. The threshold concentration of chloride ion in aqueous phase for the onset of corrosion of steel bars was set as 0.05 wt.% of concrete. It takes 2.5 years for the value of $[\mathrm{Cl}^-(\mathrm{aq})]$ at B to reach this threshold value and it takes 3 years for the case of A. However, even after 20 years, this threshold value has not been reached at C. Therefore, one can conclude that the chloride ion from the external environment is an important factor to determine the onset of corrosion of steel bars. Figs. 4 and 5 show the concentration distributions of chloride ions in aqueous and solid phases, respectively, after 20 years under the same conditions as in Fig. 3. From Fig. 4, it can be predicted that the corrosion of steel bars near the boundary Γ_1 is in progress, since the value of $[\mathrm{Cl}^-(\mathrm{aq})]$ exceeds 0.05 wt.% of concrete. Fig. 5 indicates that a large fraction of chloride ions are bound in solid phase. Hence, without the consideration of binding of chloride ions in solid phase, calculation results can be erroneous.

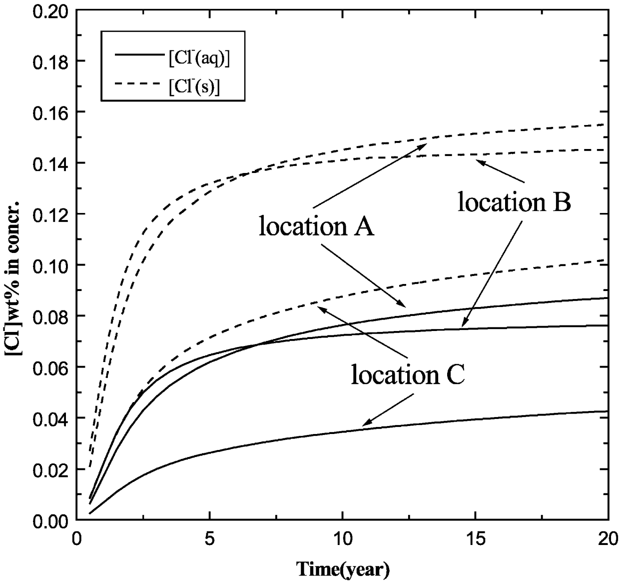


Fig. 3. Variation of chloride ion concentration with time for the case without initial presence of chloride ion.

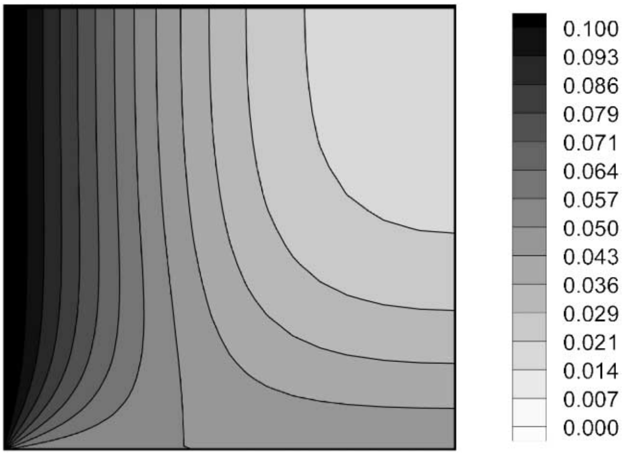


Fig. 4. Contour plot of chloride ion concentration in aqueous phase after 20 years. Conditions were as in Fig. 3.

Fig. 6 illustrates the variation of chloride ion concentrations with time for the case with 0.3 wt.% of chloride ion introduced by using marine aggregate. As compared with the case of Fig. 3, it takes less time (approximately 2 years) for the value of $[\mathrm{Cl}^-(\mathrm{aq})]$ at A and B to reach 0.05

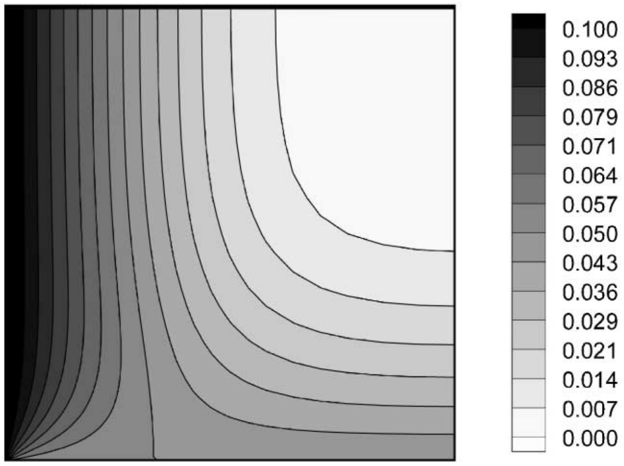


Fig. 5. Contour plot of chloride ion concentration in solid phase after 20 years. Conditions were as in Fig. 3.

wt.%. For the case of C, after 20 years, this threshold value of $[Cl^-(aq)]$ has been exceeded. These results indicate that the use of marine aggregate accelerates the corrosion of steel bars.

In order to test the validity of the modeling, the calculated results based on modeling were compared with the measured data on Fig. 7. In accordance with ASTM C 42, two drilled cores (diameter: 10 cm, length: 10 cm) were taken from two different surfaces of a support beam of a concrete bridge constructed 30 years ago in a marine area. Drilled core A was sampled on Γ_1 of Fig. 1(a) at the location 50 cm away from the corner and drilled core B on Γ_2 at the location 10 cm away from the corner. Those cores were cut laterally into 2-cm thick discs representative of the concrete core at various depths. For each disc, an average concentration of chloride ion in aqueous phase of concrete were determined by the potentiometric titration with silver nitrate as described in ASTM C 1218 and ASTM C 114. To obtain the best fit of measured data, the values of $[Cl^-(aq)]_1$ and $[Cl^-(aq)]_2$ used for calculation were 0.37 and 0.25 wt.%, respectively. The calculated profiles of chloride ion concentration are in good agreement with the measured data except the region near the surface of concrete structure. The relatively lower values of chloride ion concentration near the surface were reported previously [8]. This phenomenon may result from the fact that the repeated exposure of surface to the chloride ion source such as the spray or splash of seawater and the subsequent evaporation of water of the surface region of concrete drive the movement of chloride ion into the body of concrete. In addition, the carbonation of the surface region of concrete may cause the migration of chloride ion into the non-carbonated region of concrete [9].

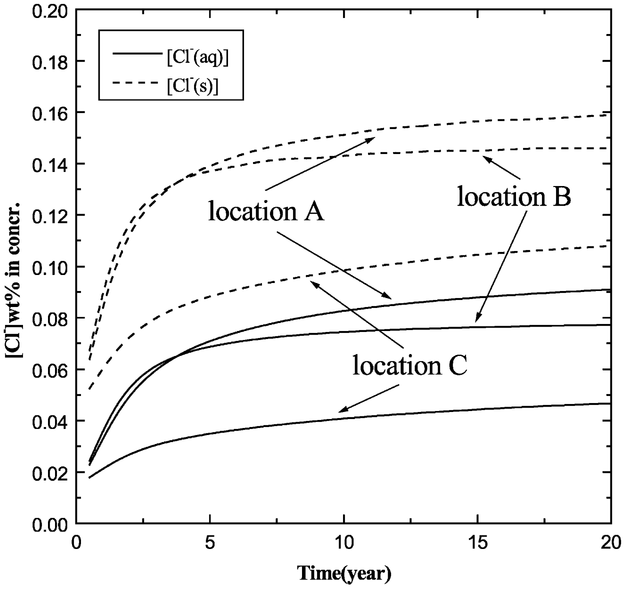
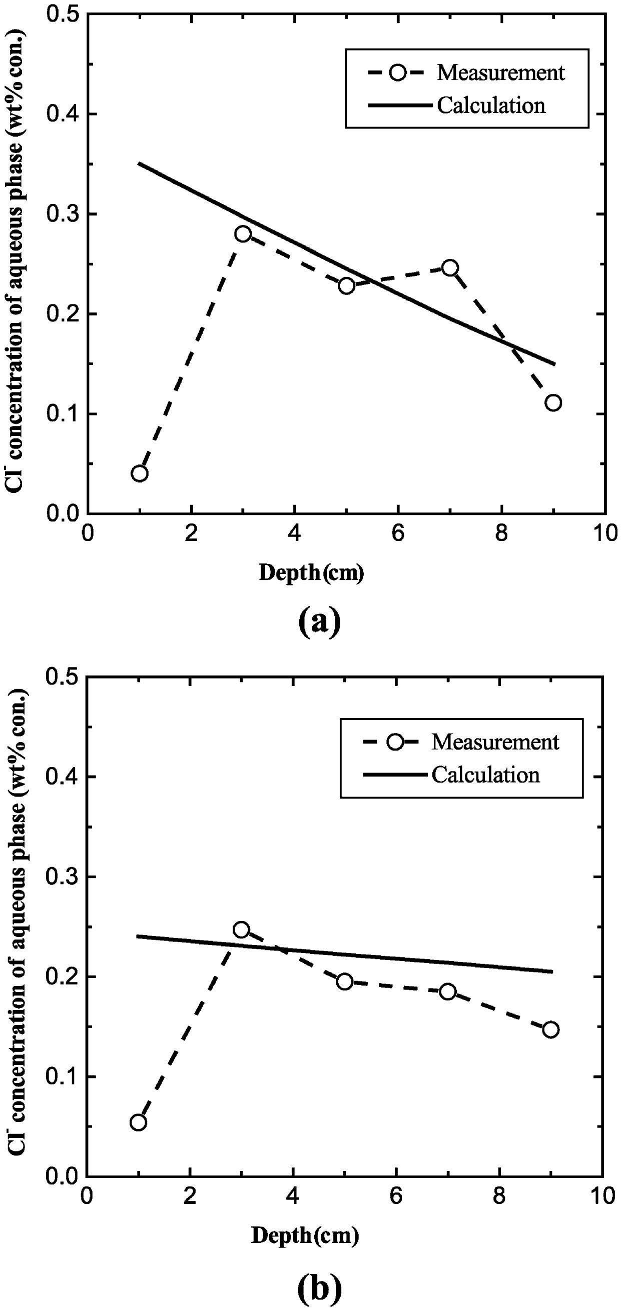


Fig. 6. Variation of chloride ion concentration with time for the case with the initial presence of chloride ion.



(a)

(b)

Fig. 7. Comparison between calculation results and measured data on the distributions of chloride ion concentration in aqueous phase of concrete for (a) drilled core A and (b) drilled core B.

5. Conclusions

A mathematical model including the diffusion of chloride ion in aqueous phase of pores, the adsorption and desorption of chloride ions to and from the surface of solid phase of concrete, and the chemical reaction of chloride ions with solid phase was presented to analyze the intrusion of chloride ion into concrete structures.

Two cases with and without the initial presence of chloride ions in the admixture at the mixing stage were studied based on the finite element method. The concentration of chloride ion at the wall of concrete structure and the amount of chloride ion contained in the admixture were identified as the main factors to determine the onset of the corrosion of steel bars. It was confirmed that a considerable fraction of chloride ions is bound in solid phase of concrete. Therefore, the binding of chloride ions in solid phase must be considered in order to describe the behavior of chloride ions penetrating into concrete structure correctly. The concentration profiles of chloride ions predicted by the model agreed favorably with the measured data.

The modeling on the ingress of chloride ion in concrete validated through the comparison with the measured data may be useful for the prediction of the onset of reinforcement corrosion and the identification of maximum limit of permissible amount of chloride ions contained in admixture.

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