

# MODELING CHLORIDE PENETRATION IN SATURATED CONCRETE

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**ABSTRACT:** A mathematical model is established for chloride penetration in saturated concrete. The model takes into account various influential parameters such as water-to-cement ratio, curing time, types of cement, and aggregate content. Two material models are developed for binding capacity and chloride diffusivity, which have a dominant effect on the chloride diffusion process. The chloride binding capacity is modeled by means of the chloride adsorption isotherm. The chloride diffusivity is modeled by a composite material theory in which concrete is considered as a two-phase material with the cement paste as one phase and the aggregate as another. To take into account the effect of aggregate content, the three-phase model for diffusivity of a two-phase composite developed by Christensen is used. The diffusivity for cement paste is characterized by the Kozeny-Carman model as modified by Martys et al. The influences of temperature and chloride ion concentration are also handled in the model. The model prediction agrees quite well with available test results.

## INTRODUCTION

Concrete is effective in protecting embedded steel from corrosion. However, when the chloride concentration in the concrete reaches a certain level, the protective environment in the concrete is destroyed, and the corrosion process starts. Therefore, chloride penetration into concrete is a critical issue in the process of corrosion of reinforcing steel bars. The problem is particularly acute in a marine environment, in bridges and roadways subjected to deicing salts, and in parking garages into which salt is transported from salted roadways.

The early attempts to model the corrosion process of steel inside concrete were focused on establishing adequate governing equations and qualitative reasoning on their implications [e.g., Halstead (1976)]. A comprehensive system of the equations governing the process of corrosion of steel in concrete was formulated by Bažant (1979a,b), but in view of insufficient test data, only simplified solutions for some elementary situations were studied. There are two approaches to formulate a model for chloride penetration. One is based on the conventional diffusion theory at the macroscopic level, that is, Fick's first law and the mass conservation (Saetta et al. 1993; Frey et al. 1994). The other is based on the basic laws of electrochemistry, particularly the Nernst-Planck equation and the Nernst-Einstein equation (Andrade 1993; Chatterji 1994).

The problem with the first approach is that the parameters in the governing differential equations are all effective parameters at large scale, which means they are averaged parameters over a representative volume. To take into account the chemical and physical mechanisms that occur at small scales, various simplified formulas have been assumed, and accordingly many empirical parameters have been intuitively introduced in the formulas. The resulting models, therefore, do not provide a clear understanding of each individual diffusion mechanism of the process. The problem with the second approach is opposite. The basic equations retain at the molecular (nanometer) level and a jump must then be made over six orders of magnitude to compare with test results at the millimeter level. It is difficult for the approach to take into account the effect of concrete internal structure, such as the effects of aggregate and pore structure of cement paste. In any case, no matter which

approach is used for formulating the governing equations, determination of the material parameters in the equations is overwhelmingly important. This is the major focus of the present study.

When chloride ions enter concrete, some of them will be bound to the internal surface of cement paste and aggregate. They are called bound chloride. The others, called free chloride, diffuse freely through the concrete. Research has shown that steel corrosion is related only to the free chloride content but not the total chloride content. So the governing equation should be expressed in terms of the free chloride content. For saturated concrete, the diffusion process is driven by concentration gradient of chloride ions. The governing equation is

$$\frac{dC_f}{dt} = \frac{dC_f}{dC_t} \text{div}[D_{Cl} \text{grad}(C_f)] \quad (1)$$

where  $C_t$  = total chloride concentration, in grams of total chloride per gram of concrete (g/g);  $C_f$  = free chloride concentration, in grams of free chloride per gram of concrete (g/g);  $t$  = time, in days;  $D_{Cl}$  = chloride diffusivity; and  $dC_f/dC_t$  = binding capacity. In this study, the weight ratios of chloride to concrete,  $C_f$  and  $C_t$ , are used because they are the commonly used unit system for the evaluation of chloride content in the concrete industry (Cady and Weyers 1983, 1992; Funahashi 1990).

The two material parameters, the binding capacity and the chloride diffusivity, must be determined first before the field equation can be solved. Eq. (1) is formulated on the basis of Fick's first law and mass conservation. It is valid at different scales as long as the two material parameters have correct physical meanings. On the microscopic scale, the equation holds at a point in space and the parameters in the equation must represent properties of a single phase when the point is located in that phase. On the meso-scale, the equation holds for the representative volume of the composite and the two parameters must be the effective properties of the composite. The present study treats concrete as a composite material, and thus the two material parameters must be the effective properties of the concrete.

Since chloride diffusion is a very complicated process, material properties other than the binding capacity and diffusivity are involved. To avoid curve fitting and lumping all the physical and chemical mechanisms into one oversimplified equation, a proper material model will be developed for each material property involved. Each of these models will be calibrated on the basis of its own test data. In this manner, each material parameter will have clear physical meaning. This is the major difference from previous studies.

The framework of this study was briefly presented in a conference paper (Xi 1997) without giving details about the de-

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termination of model parameters and comparison with available test results.

## BINDING CAPACITY $dC_b/dC_f$

The binding capacity is defined as the relationship between the change of total chloride concentration and a change of free chloride concentration. The total chloride concentration is the sum of the bound and the free chlorides. Therefore, the binding capacity can be expressed as follows in terms of  $dC_b/dC_f$ :

$$C_t = C_f + C_b; \quad \frac{dC_f}{dC_t} = \frac{1}{1 + (dC_b/dC_f)} \quad (2)$$

where  $C_b$  = bound chloride concentration, in grams of bound chloride per gram of concrete; and  $C_b$  is an effective parameter for concrete, which includes the bound chloride in the cement paste and in the aggregates. Although  $dC_f/dC_t$  is defined in the present study as the binding capacity, it is  $dC_b/dC_f$  rather than  $dC_f/dC_t$  that represents the ratio of the increments of bound chloride and free chloride. What one needs to know in (2) is  $dC_b/dC_f$ , which is called the chloride isotherm. It has been obtained experimentally.

As one can see from (1) and (2), the lower the value of  $dC_f/dC_t$ , the slower the process of chloride penetration. So, binding capacity and chloride diffusivity play equally important roles in the process of chloride penetration. The bound chloride ions in concrete are either physically adsorbed on the surface of pore walls or trapped in the pores, or chemically reacted with certain components of portland cement paste. For instance, Midgley and Illston (1984) found that chloride ions react with some of the hydration products, in particular the tricalcium aluminate and the ferrite phase ( $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{FeO}$ ), and combine to form Friedel's salt ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ ), which is insoluble in water.

## Chloride Isotherm

Tang and Nilson (1993) established the relationship between the free chloride and the bound chloride based on the so-called Freundlich isotherm

$$\log(C'_b) = A \log(C'_f) + B \quad \text{or} \quad C'_b = (C'_f)^A 10^B \quad (3)$$

where  $A$  and  $B$  = two material constants related to chloride adsorption; and  $C'_b$  and  $C'_f$  = bound and free chloride concentrations, respectively, but in a unit system differing from  $C_b$  and  $C_f$ .  $C'_b$  is in milligrams of bound chloride per gram of calcium silicate hydrate (C-S-H) gel (mg/g); and  $C'_f$  is in moles of free chloride per liter of pore solution (mol/L). The advantage of using such a unit system is that the resulting Freundlich isotherm is independent of the water-to-cement ratio and the aggregate content of concrete because it is based on amounts of C-S-H gel and pore solution. However, for practical engineering problems, it is necessary to use the unit system defined for  $C_b$  and  $C_f$ , because the amounts of C-S-H gel and the pore solution vary with the hydration process and are not easy to measure in regular laboratories.

For this purpose, one needs to convert (3) into the unit system adopted in (1), and then determine the binding capacity. Considering  $C'_f$  first, the molecular weight of chlorine is 35.45 g/mol, and by introducing a conversion factor  $\beta_{\text{sol}}$ , one has the relationship between  $C_f$  and  $C'_f$

$$C_f = 35.45\beta_{\text{sol}}C'_f \quad (4)$$

where  $\beta_{\text{sol}}$  = ratio of pore solution to concrete, in liters of the pore solution per gram of the concrete (L/g). In the same manner, introducing a conversion factor  $\beta_{\text{C-S-H}}$ , one has the relationship between  $C_b$  and  $C'_b$

$$C_b = \frac{\beta_{\text{C-S-H}}D'_b}{1,000} \quad (5)$$

where  $\beta_{\text{C-S-H}}$  = ratio of C-S-H gel to concrete, in grams of C-S-H gel per gram of concrete (g/g). Substituting (4) and (5) into (3) gives

$$C_b = \frac{\beta_{\text{C-S-H}}}{1,000} \left( \frac{C_f}{35.45\beta_{\text{sol}}} \right)^A 10^B \quad (6)$$

The test results of Tang and Nilsson (1993) showed that parameter  $A$  in (6) is not equal to one, which means the binding isotherm is essentially nonlinear in nature. Their test results have been supported by some recent reports (Delagrave et al. 1997b; Ollivier et al. 1997). From (6), the binding capacity can be evaluated

$$\frac{dC_f}{dC_t} = \frac{1}{1 + (A10^B\beta_{\text{C-S-H}}/35.450\beta_{\text{sol}})(C_f/35.45\beta_{\text{sol}})^{A-1}} \quad (7)$$

From this equation it is clear that  $\beta_{\text{sol}}$  and  $\beta_{\text{C-S-H}}$  are the two important parameters for evaluating the binding capacity.

## Parameter $\beta_{\text{sol}}$

From the definition of  $\beta_{\text{sol}}$ , one has

$$\beta_{\text{sol}} = \frac{V_{\text{sol}}}{W_{\text{conc}}} = \frac{W_{\text{sol}}}{\rho_{\text{sol}}W_{\text{conc}}} = \frac{n(H, T)}{\rho_{\text{sol}}} \quad (8)$$

where  $\rho_{\text{sol}}$  = density of the solution (g/L);  $V_{\text{sol}}$  and  $W_{\text{sol}}$  = volume and weight of the pore solution, respectively;  $W_{\text{conc}}$  = weight of the concrete; and  $n(H, T) = W_{\text{sol}}/W_{\text{conc}}$ , which is the ratio of the weight of pore solution to the weight of concrete.  $n(H, T)$  is a function of temperature,  $T$ , and relative humidity,  $H$ . For saturated concrete,  $H = 1.0$ . In the present study, the focus is on saturated concrete only, and both  $H$  and  $T$  are kept constant. Nevertheless, both saturated concrete and nonsaturated concrete can be included in  $n(H, T)$  in its general form.

From (8), one can see that  $\beta_{\text{sol}}$  depends on the density of the solution,  $\rho_{\text{sol}}$ , and  $n(H, T)$ .  $\rho_{\text{sol}}$  depends, in turn, on the chloride concentration, which is the unknown one is looking for. Actually, in concrete, the density of pore solution varies in a very limited range, and thus, to simplify the problem,  $\rho_{\text{sol}}$  can be considered to be the density of pore water. On the other hand,  $n(H, T)$  depends on  $H$ ,  $T$ , and the pore structure. The pore structure, in turn, depends on  $H$  and  $T$ , as well as the age of concrete. Due to a lack of test data on chloride isotherm,  $n(H, T)$  may be considered to be the isotherm of water adsorption rather than the adsorption isotherm of chloride solution. The adsorption of water has been studied extensively, and a semiempirical model has recently been established based on BET theory and water adsorption test results for cement paste (Xi et al. 1994; Xi 1995b).

The aggregate occupies about 50% of the volume of concrete, and its effect on the binding capacity cannot be underestimated. The BET theory can also be used for aggregates, and a model for the three BET parameters for aggregate has also been developed (Xi 1995a). By combining adsorption isotherms of cement paste and aggregate, the effective adsorption isotherm for concrete may be obtained as follows:

$$n(H, T) = f_{\text{cp}}n_{\text{cp}}(H, T) + f_{\text{agg}}n_{\text{agg}}(H, T) \quad (9)$$

where  $f_{\text{cp}}$  and  $f_{\text{agg}}$  are weight percentages of cement paste and aggregate, respectively; and  $n_{\text{cp}}(H, T)$  and  $n_{\text{agg}}(H, T)$  = adsorption isotherm of cement paste and aggregate, respectively. Eq. (9) considers only the weight average of the isotherms of the two constituents. Interactions with other material parameters are not included. A more sophisticated treatment of this problem can be found elsewhere (Xi 1995b).

## Parameter $\beta_{C-S-H}$

A recently developed model for the process of cement hydration based on cement chemistry and on analyses of the micrographs of a scanning electron microscope (Jennings and Tennis 1994) is used in the present study. The model considers five different phases of cement paste: anhydrous, inner hydration product, outer hydration product, capillary pores, and calcium hydroxide (CH and other AFm phases). Jennings and Tennis's model has been rearranged to fit the need of the present formulation. The volume of C-S-H in the present formulation is the sum of the inner and outer products;  $V_{C-S-H} = V_{inner} + V_{outer}$ . The volume fraction of C-S-H is

$$f_{C-S-H} = \frac{V_{C-S-H}}{V_{total}} = \frac{V_{total} - V_1 - V_{cp}}{V_{total}} = 1 - f_1 - f_{cp} \quad (10)$$

where  $V_{total}$  = total volume, which is assumed to be a constant;  $V_{cp}$  = volume of capillary pores; and  $V_1$  and  $f_1$  = volume and volume fraction of the anhydrous cores of cement grains and of all the crystalline phases, such as CH and ettringite. The detailed calculation can be seen in Jennings and Tennis (1994).

When the volume fraction of C-S-H is calculated from (10), it needs to be converted to the weight ratio of C-S-H since  $\beta_{C-S-H}$  is defined in grams of C-S-H gel per gram of concrete. The typical values of specific gravities of concrete and C-S-H are very close (2.3 and 2.34), and so  $\beta_{C-S-H} \approx f_{C-S-H}$  without significant loss of precision.

From the foregoing analysis on  $\beta_{C-S-H}$  and  $\beta_{sol}$ , one can see that  $\beta_{C-S-H}$  determines the effect of cement composition and age on the volume fraction of C-S-H, while  $\beta_{sol}$  represents the effect of the structure of hydration products because for the same  $\beta_{C-S-H}$  the difference in internal structure of C-S-H makes  $\beta_{sol}$  different. Delagrave et al. (1997a) have shown that the hydrated cement paste binding capacity is predominantly influenced by the amount of C-S-H gel, and that parameters such as the type of cement play only a secondary role.

## CHLORIDE DIFFUSIVITY

Several important parameters affect chloride diffusivity significantly. These parameters will be first discussed and formulated separately and then combined together.

### Effect of Aggregates

The effective diffusivity of concrete can be obtained by means of the theory of composite materials. Christensen (1979) developed a composite model for diffusivity based on the three-phase model and Fick's first law. When diffusivities of cement paste and aggregate are obtained, the effective diffusivity of concrete can be evaluated on the basis of the composite sphere model (Christensen 1979)

$$D_{eff} = D_m \left\{ 1 + \frac{g_i}{[(1 - g_i)/3] + [D_m/(D_i - D_m)]} \right\} \quad (11)$$

where  $D_i$  and  $D_m$  = diffusivities of inclusions (aggregate) and matrix (cement paste), respectively;  $g_i$  = volume fraction of the inclusions; and  $D_{eff}$  = effective diffusivity, which depends on the configuration of the two constituent phases, the microstructural features of each phase, and other factors, which will be included later.

In addition to the composition effect, the interface transition zone (ITZ) between the aggregate and the surrounding cement paste has been considered to be very important for all kinds of properties of concrete. The ITZ has a higher porosity and thus a higher diffusivity than the bulk cement paste. One can imagine that, with increasing aggregate content, the ITZs around neighboring aggregates will become closer and closer

to each other, and at a certain volume fraction of aggregate, the ITZs may eventually connect with each other and thus create a continuous pathway with high porosity, although the aggregates themselves may not be mutually in contact. This particular volume fraction has been experimentally studied by mercury intrusion tests on concretes with various aggregate contents (Winslow et al. 1994). The results showed that the continuous pathway is formed at 50% or sometimes even lower aggregate contents. On the other hand, in normal concretes, the aggregate volume fraction is almost always higher than 50%, which means that most of the cement paste in concrete is in ITZs. This unveils one important fact. The cement paste matrix inside concrete is not the same material as the pure cement paste because of the disturbance of the large amount of added aggregates.

Test results (Sujata et al. 1996; Neubauer et al. 1997) showed that the thickness of the high porosity zone, or ITZ, varies randomly around the perimeters of aggregates. It depends on the aggregate size, average spacing between aggregates, and surface condition of the aggregate particles. Therefore, the properties obtained from the tests of pure cement paste should not be applied directly to the cement paste matrix in concrete. According to the foregoing analysis, when the aggregate content is low, the matrix is composed of bulk cement paste as well as ITZs, and the properties of the matrix should be considered as a function of the added aggregate content. When the aggregate content is high (e.g., above 50%), most of the matrix is ITZs, and thus the properties of cement paste may be considered as constants. The present study focuses on the high aggregate content used in most practical concrete mix designs; the properties of cement paste matrix are taken to be constants.

### Microstructural Dependence in $D_i$ and $D_m$

The diffusivity of porous materials, in general, can be estimated by the Kozeny-Carman equation (Carman 1956) involving pore volume and internal surface area

$$D = \frac{V_p^3}{S^2 K_k} \quad (12)$$

where  $D$  = diffusivity, which can be  $D_i$  or  $D_m$ ;  $V_p$  = porosity;  $S$  = specific surface area (surface area/bulk volume); and  $K_k$  = Kozeny constant =  $K_t \times K_s$ , where  $K_t$  = tortuosity of the microstructure, and  $K_s$  = shape factor of pores. The appeal of the Kozeny-Carman equation is its simple form and its good prediction power for flows through powders in chemical engineering. Criticisms of its application to cementitious materials have been mainly two: (1) Not all of the porosity is available for transport of moisture, chloride, or other chemicals; and (2) the specific surface area (measured by water or nitrogen adsorption) almost always overestimates the relevant length scale for fluid flow (Garboczi 1990). This is because cementitious materials usually have an extremely high surface area, due to the complicated structure of C-S-H gel on a very fine scale, but pore sizes, relevant to chloride diffusion, are not significantly affected by such fine scale pores.

One possible modification of the Kozeny-Carman equation is that only the relevant porosity and the corresponding surface area are included in the equation. In this sense, the porosity and the specific surface area in (12) are not those measured by water adsorption or mercury intrusion tests, but only a part of them. Martys et al. (1994) suggested introducing the critical porosity,  $V_p^c$ , into the Kozeny-Carman equation.  $V_p^c$  is the porosity at which the pore space is first percolated. The physical meaning of  $V_p^c$  is similar to the critical pore diameter,  $d_c$ , defined in the Katz-Thompson theory (Katz and Thompson 1986, 1987).  $d_c$  has been linked to the inflection point in the cu-

mulative intrusion curve obtained from mercury intrusion test. Martys et al. (1994) proposed

$$D = \frac{2[1 - (V_p - V_p^c)]}{S^2} (V_p - V_p^c)^f \quad (13)$$

where  $f = 4.2$ . The important parameter in (13) is  $V_p^c$ . Numerical simulation of porous materials composed of randomly overlapping spheres showed that the pore space becomes disconnected at  $V_p^c = 3\%$  (Martys et al. 1994). Connectivity of the microstructure of cement paste is much more complicated than that of randomly overlapping spheres. Thus, it would not be surprising if  $V_p^c$  for cement paste were higher than 3%, but so far, no test data are available in this respect. Estimations of surface area  $S$  and porosity  $V_p$  of cement paste are given later.

### Temperature Dependence

Temperature has a significant effect on the rate of diffusion in more than one respect. First of all, temperature changes the adsorption heat, and this effect has been included in BET adsorption isotherms [(9)]. Secondly, temperature increases the frequency of thermal vibrations of the diffusant, which can be taken into account by the Arrhenius's law

$$D_T = D_0 \exp \left[ \frac{U}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (14)$$

where  $T_0$  and  $T$  = reference temperature and current temperature, respectively ( $^{\circ}\text{K}$ );  $D_T$  = diffusivity at the temperature  $T$ ;  $D_0$  = diffusivity at the reference temperature  $T_0$ ;  $R$  = gas constant; and  $U$  = activation energy of the diffusion process.  $U$  has been found to depend on water-to-cement ratio  $w/c$  and on the cement type (Page et al. 1981; Collepardi et al. 1972). Some test results on the values of  $U$  for various  $w/c$  are shown in Table 1.

### Concentration Dependence

Chloride diffusivity is concentration dependent, which makes the governing equations [(1)] nonlinear. The Kozeny-Carman equation is valid in principle for an undissociated diffusant, and thus the major resistance to the diffusion process is due to the wall effect, i.e., interaction of the diffusant with the pore wall. However, for the diffusion of ions, especially diffusion of chloride ions in the present study, the movement of ions is restricted by the electrostatic field induced by the other ions present in the solution. This restriction can be expressed by the following equation (Moore 1978; Chatterji 1994):

$$D_{\text{ion}} = \frac{kTU}{Z_{\text{ion}}e} \quad (15)$$

where  $D_{\text{ion}}$  = ionic diffusivity;  $k$  = Boltzmann constant;  $Z_{\text{ion}}$  = valency of the ion; and  $e$  = electric charge. The equation can also be expressed in another way.

$$D_{\text{ion}} = \frac{RT\Lambda_{\text{ion}}}{F^2|Z_{\text{ion}}|} \quad (16)$$

where  $F$  = Faraday constant; and  $\Lambda_{\text{ion}}$  = molar conductance of the ions.  $\Lambda_{\text{ion}}$  and the free ion concentration  $C_f$  have an empirical relationship:

$$\Lambda_{\text{ion}} = \Lambda_0 - k_c(C_f)^m \quad (17)$$

where  $\Lambda_0$  = reference conductance; and  $k_c$  and  $m$  = two positive constants. From (16) and (17), it is clear that chloride diffusivity is concentration dependent, and with increasing  $C_f$ , the diffusivity decreases. Under isothermal conditions and for diffusion of only one type of ion,  $T$ ,  $F$ ,  $\Lambda_0$  and  $Z_{\text{ion}}$  are all constants, and (16) and (17) may then be rewritten

$$D_{\text{ion}} = D'[1 - k_{\text{ion}}(C_f)^m] \quad (18)$$

where  $D' = RT\Lambda_0/F^2|Z_{\text{ion}}|$ ; and  $k_{\text{ion}} = k_c/\Lambda_0$ . It should be pointed out that there must be a lower limit for (18). Otherwise, when  $C_f$  reaches certain value,  $D_{\text{ion}}$  will take zero or even negative values. Nevertheless, this is not a problem in the present study because  $C_f$  is a very small number as is defined in terms of the weight of concrete.

### General Expression for Chloride Diffusivity

The general expression for chloride diffusivity can be written by combining (11) with (18)

$$D_{\text{Cl}} = f_{\text{Cl}} D_m \left\{ 1 + \frac{g_i}{[(1 - g_i)/3] + [1/(D_i/D_m - 1)]} \right\} \cdot \exp \left[ \frac{U}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] [1 - k_{\text{ion}}(C_f)^m] \quad (19)$$

where  $f_{\text{Cl}}$  = factor taking into account all the constants in (11)–(18). Also,  $f_{\text{Cl}}$  includes all the other influential parameters that are not considered in (19) (see the next section for detailed discussion). The value of  $D_i$  can be evaluated by (13) (if  $S$ ,  $V_p$ , and  $V_p^c$  for the aggregate are known) or may be taken simply as a constant, typically  $1 \times 10^{-12}$  cm/s.  $D_m$  can be evaluated from (13), in which the surface area of cement paste,  $S$ , can be estimated by the monolayer capacity  $V_m$  of adsorption isotherm of concrete since  $V_m$  is proportional to  $S$  (Xi et al. 1994; Xi 1995b). Porosity  $V_p$  for cement paste can be estimated by using the adsorption isotherm at saturation ( $H = 1$ ). It should be noted that  $n(H, T)$  is defined as a weight ratio and needs to be converted into a volume fraction.

## PARAMETERS INFLUENCING CHLORIDE BINDING CAPACITY AND DIFFUSIVITY

### Chloride Binding Capacity

The present model can be used to predict the effect of various influencing parameters on the binding capacity of chloride. Fig. 1 shows the effect of water-cement ratio on  $dC_b/dC_f$ , calculated at saturation state for various curing periods, in which parameter  $A = 0.3788$  and  $B = 1.14$  (Tang and Nilsson 1993). One can see that, with increasing  $w/c$ ,  $dC_b/dC_f$  increases. This is because the higher the  $w/c$  (at fixed curing time and same type of cement), the larger the volume fraction of capillary pores. Consequently, the increment of the free chloride content in a saturated pore solution is larger after a change in the total chloride content. Fig. 2 shows the predicted curves of  $dC_b/dC_f$  along with the effects of water-cement ratio and curing time [from (2),  $dC_b/dC_f = 1 - dC_f/dC_i$ ]. One can see that, with increasing  $w/c$ ,  $dC_b/dC_f$  decreases. The effect of curing time can be seen from both Figs. 1 and 2. With the same water-cement ratio, a longer curing time corresponds to a higher degree of maturity of C-S-H gel (a higher surface

TABLE 1. Activation Energies for Various Cement Pastes

$w/c$ (1)	$U$	
	Ordinary portland cement (KJ/mol) (2)	Cement with pozzolans (KJ/mol) (3)
0.4	41.8 $\pm$ 4.0	—
0.5	44.6 $\pm$ 4.3	4.18
0.6	32.0 $\pm$ 2.4	—

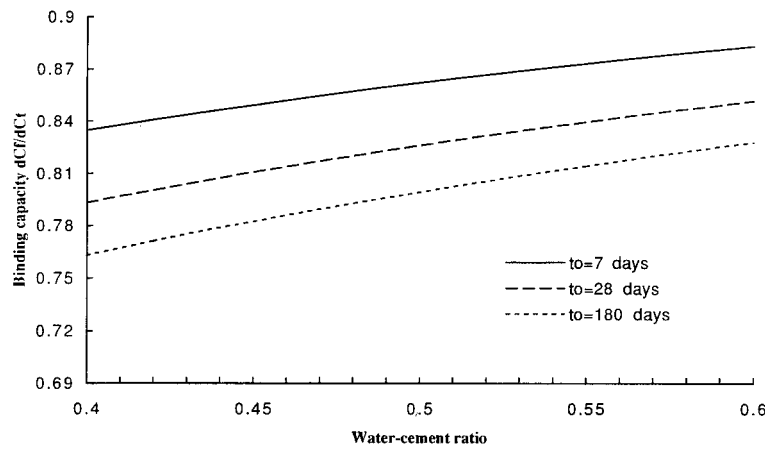


FIG. 1. Effects of Water-Cement Ratio and Curing Times on Binding Capacity  $dC_f/dC_t$

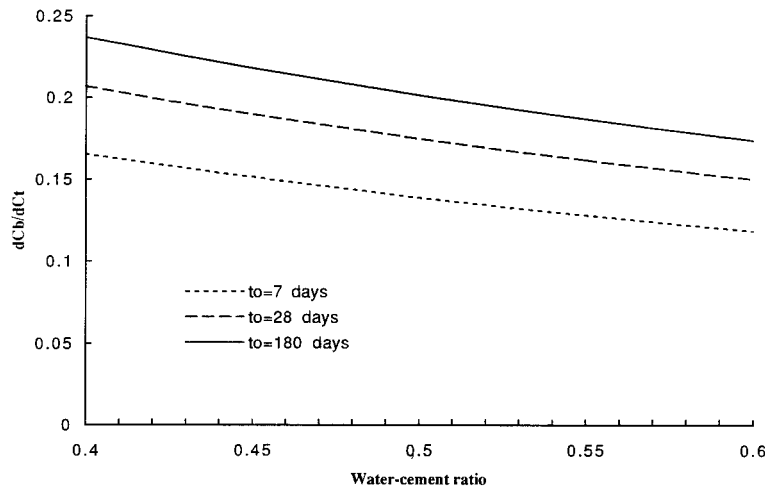


FIG. 2. Effects of Water-Cement Ratio and Curing Times on  $dC_b/dC_t$

area and a higher tortuosity of the microstructure). This means more of bound chloride and thus a higher  $dC_b/dC_t$ .

There are other influencing parameters that have not been included in the present model. For instance, research has shown that the inclusion of pozzolanic materials, such as silica fume and fly ash, changes the  $C/S$  ratio, which then results in an increase of  $C_f$  (Byfors 1987; Beaudoin et al. 1990). All these influences can be taken into account by the two parameters,  $A$  and  $B$ , in the Freundlich isotherm [(3) and (7)]. Although the basic trends of these influencing parameters have been known, the quantitative correlation between these parameters and the isotherm has not been understood well. No systematic test results are available. Therefore, these parameters are not included in the present study.

### Chloride Diffusivity

Fig. 3 shows the effect of water-cement ratio on chloride diffusivity for various curing periods as predicted by the present model. The curves are calculated for 5% of NaCl concentration in the pore solution. One can see that, with increasing  $w/c$ , the diffusivity increases. This is because a higher  $w/c$  (for a fixed curing time and the same type of cement) leads to a higher volume fraction of capillary pores, and consequently a higher value of the diffusivity. With the same water-cement ratio, a longer curing time corresponds to a higher degree of maturity of C-S-H gel (and a higher tortuosity of the pore system), which in turn means lower diffusivity.

Fig. 4 shows the effect of aggregate content on the diffusivity. The lowest aggregate content considered in the model is taken to be 50%, as explained previously. Above this level

of aggregate content, the diffusivity of cement paste may be considered as constant. The water-cement ratio in Fig. 4 is 0.55, and the curing time is 7 days. The assumption adopted in this example is that the aggregate has a much lower diffusivity than the cement paste. Therefore, with an increasing volume fraction of aggregate, the ratio of the effective diffusivity of concrete to the diffusivity of cement paste decreases. For a given cement paste, the magnitude of the reduction in the effective diffusivity depends on the diffusivity of the aggregate used.

There are some other parameters affecting the diffusivity of chloride. For example, the relative humidity has a significant effect on the diffusivity of nonsaturated concrete. The present study is restricted to the case of total saturation, i.e.,  $H = 1.0$ . Research also shows that the diffusivity in the surface layer of a concrete specimen is lower than inside. The reason is that  $\text{CaCO}_3$ , a product of the carbonation process, blocks the pores in the surface layers, which decreases the diffusivity. For this reason, some previous studies (Tang and Nilsson 1994) assumed the diffusivity as a function of the depth from the concrete surface. On the other hand, the superficial layer of concrete is mostly made of cement paste, which often tends to be more porous than bulk concrete (Kreijer 1984), which leads to a high diffusivity. They also regularly subjected to wetting and drying cycles that tend to induce microcracks and alter the hydrated cement paste pore structure, which also results in a high diffusivity. Nevertheless, the diffusivity of concrete depends on the environmental conditions and on the microstructure of cement paste and aggregates. In other words, the effect of the environment (such as temperature, drying, and carbonation) varies from concrete to concrete. Diffusivity, as a gen-

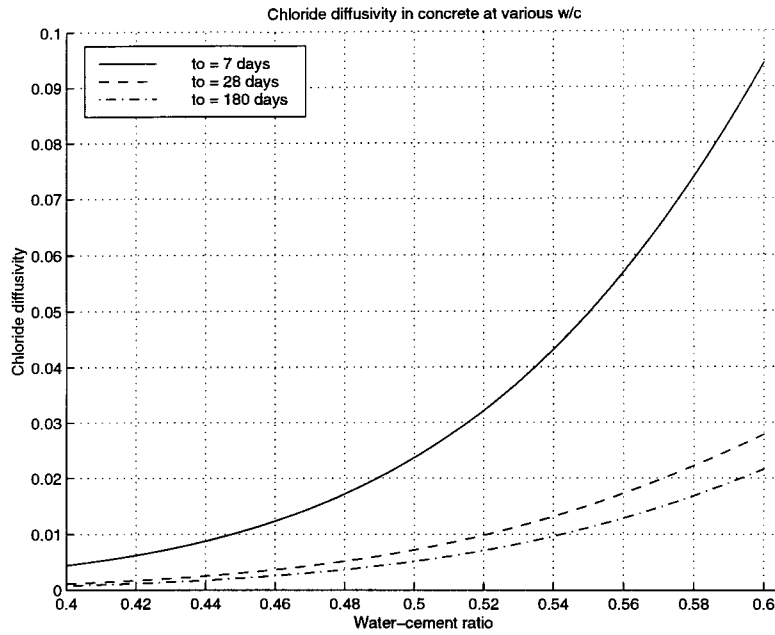


FIG. 3. Chloride Diffusivity of Concrete at Various Water-Cement Ratio and Curing Times

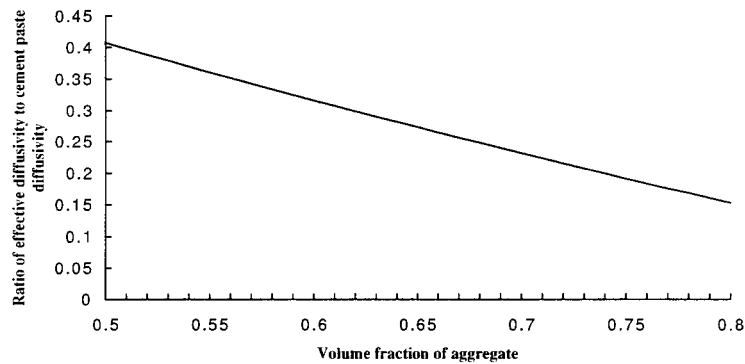


FIG. 4. Effect of Aggregate Content on Diffusivity ( $wk = 0.55$ ;  $t_0 = 7$  days)

eral material property, cannot be modeled as a function of the location of the material element in the structure.

## NUMERICAL SOLUTION AND COMPARISON WITH TEST RESULTS

Most chloride diffusion problems can be treated as one-dimensional, e.g., chloride penetration into a pavement or bridge deck. The one-dimensional form of (1) is

$$\frac{dC_f}{dt} = \frac{dC_f}{dx} \frac{d}{dx} \left( D_{Cl} \frac{dC_f}{dx} \right) \quad (20)$$

with initial and boundary conditions  $C_f = C_{ini}$  for  $t = t_0$ ;  $C_f = C_{en}$  for  $x = L$ ; and  $dC_f/dx = 0$  for  $x = 0$ .  $C_{ini}$  is the initial free chloride concentration in concrete;  $C_{en}$  is the environmental concentration in the same units as  $C_f$ ; and  $L$  is the length or depth of concrete specimen along the direction of chloride penetration. Depending on the available test data of the initial and environmental concentrations, conversion of the unit systems may be needed. For instance, if the measured environmental concentration,  $C_0$ , is in grams of chloride per liter of the solution (g/L), then  $C_{en} = C_0 \beta_{sol}$ , where  $\beta_{sol}$  is computed by using (8) and (9) and taking  $t = t_0$ ,  $H = 1$  (saturation). All the other parameters in (8) and (9) are the same as those for the concrete sample.  $C_{ini}$  can be converted by the same method.

For convenience, (20) can be normalized into a dimensionless form by setting  $x = \xi L$ ,  $t = t_0 + \tau L^2$ , and  $C_f = C_{en} + (C_{ini} - C_{en})C$ , where  $\xi$ ,  $\tau$ , and  $C$  are the normalized coordinate,

time, and chloride concentration, respectively. Once the binding capacity and chloride diffusivity are determined, the normalized (20) can be solved by a proper numerical method, such as the finite-element method or finite-difference method. In the present study, (20) is solved for the one-dimensional case by the Crank-Nicolson finite-difference algorithm (von Rosenberg 1969). The diffusion equation in a polar coordinate system is also solved by the finite-difference method and can be used to predict the distribution of chloride concentration in concrete cylinders.

In the foregoing formulation, there are not many free parameters that can be manipulated to fit the chloride diffusion test data. As one can see,  $m$  and  $k_{ion}$  in (19) and  $V_p^c$  in (12) are not precisely known. In the present study,  $V_p^c$  is taken to be a constant,  $V_p^c = 0.03$ , based on the results of computer simulations described earlier. From preliminary computations and comparisons with test results, the two other parameters,  $m$  and  $k_{ion}$ , are taken to be two constants with the values  $m = 0.5$  and  $k_{ion} = \sqrt{70}$ . Then the only parameter to be determined is  $f_{Cl}$ , which is the factor taking into account all the physical constants in (11)–(18). Also,  $f_{Cl}$  includes all the other influencing parameters that are not considered in (19) due to lack of experimental results.  $f_{Cl}$  is apparently a function of the water-to-cement ratio and the age of cement paste. In the present study, the following formula for  $f_{Cl}$  has been chosen:

$$f_{Cl} = \left[ \frac{1}{4} + \frac{(28 - t_0)}{300} \right] \left( \frac{w}{c} \right)^{6.55} + \frac{28 - t_0}{62,500} \quad (21)$$

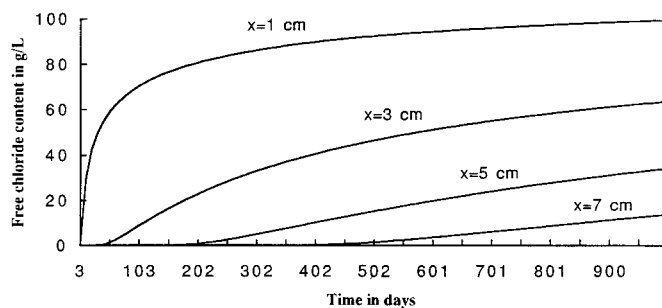


FIG. 5. Predicted Profile of Free Chloride Concentration in Concrete Specimen

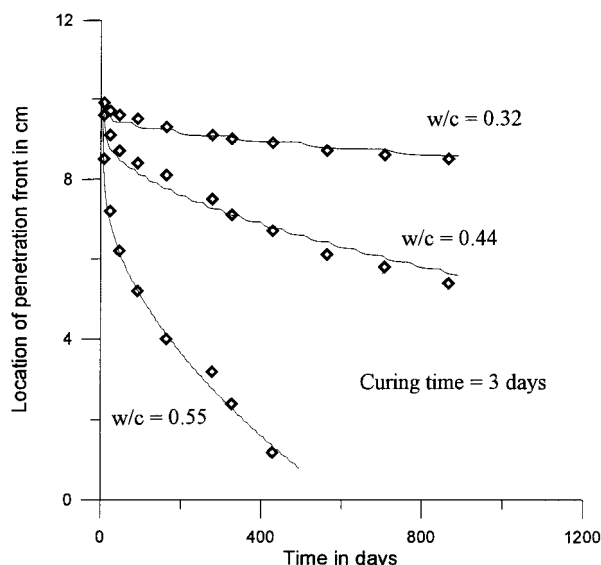


FIG. 6. Chloride Penetration Front in Concrete Specimens,  $t_0 = 3$  days

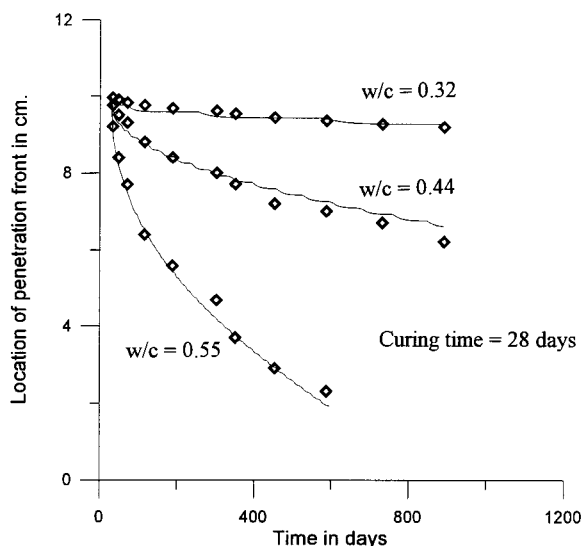


FIG. 7. Chloride Penetration Front in Concrete Specimens,  $t_0 = 28$  days

Eq. (21) is valid for concrete with  $t_0 \leq 28$  days; for concrete with  $t_0 > 28$  days,  $f_{Cl}$  can be approximately taken as the value of  $t_0 = 28$  days. The profile of free chloride concentration in a concrete specimen predicted by the present model is shown in Fig. 5. The water-to-cement ratio of the concrete is 0.55 and type I cement is used. After three days of curing, the specimen is immersed in a  $\text{CaCl}_2$  solution with chloride concentration of 10%. Figs. 6 and 7 show the comparisons of our model predictions and test results for the penetration depth of

concrete specimens of various water-to-cement ratios and different curing periods. The penetration front is defined by reaching concentration of 0.07%. The origin of the coordinate system used in the computation is located at the side opposite to the exposed surface. The dimension of the specimen in the direction of chloride penetration is 10 cm, so at the beginning of the penetration process, the penetration front is right at 10 cm. As one can see, the predictions of the present numerical model agree with the test data quite well.

## CONCLUSIONS

1. Chloride penetration into concrete can be modeled by a diffusion equation formulated in terms of free chloride concentration on the basis of Fick's first law. The equation involves two material parameters. One is the chloride binding capacity and the other is the chloride diffusivity. To avoid curve fitting and lumping up all physical and chemical mechanisms involved into a few oversimplified equations, proper material models are developed for each mechanism and calibrated by test data.
2. The chloride binding capacity is modeled by means of the chloride adsorption isotherm, which is affected by many parameters. Two parameters,  $\beta_{sol}$  and  $\beta_{C-S-H}$ , are important for evaluating the binding capacity.  $\beta_{C-S-H}$  is the ratio of the C-S-H gel to concrete, in grams of C-S-H gel per gram of concrete. It determines the effect of cement composition and age on the volume fraction of C-S-H.  $\beta_{C-S-H}$  is characterized by a microstructural model based on the chemical reaction of hydration.  $\beta_{sol}$  is the ratio of pore solution to concrete, in liters of the pore solution per gram of concrete. It represents the effect of the microstructure of hydration products because, for the same  $\beta_{C-S-H}$ , differences in internal structure of C-S-H make  $\beta_{sol}$  different.  $\beta_{sol}$  is estimated by means of a model for moisture capacity of cement paste, and is calibrated by moisture adsorption test results. The model includes the effects of water-to-cement ratio, curing temperature, curing time, and type of cement used.
3. The chloride diffusivity is modeled by a composite material theory in which concrete is considered as a two-phase material with the cement paste as one phase and the aggregate as another. To take into account the effect of aggregate content, the three-phase model for diffusivity of a two-phase composite developed by Christensen (1979) is used. The diffusivity for cement paste is characterized by the Kozeny-Carman model as modified by Martys et al. (1994), in which the effects of the surface area and the effective porosity of cement paste are included. The influences of temperature and chloride ion concentration are also handled in the model.
4. The basic trends of chloride binding capacity and diffusivity can be predicted by the present model successfully. With increasing  $w/c$ , both the diffusivity and the free chloride content increase. This is due to the fact that, at higher  $w/c$  (and fixed curing time, same type of cement), the volume fraction of capillary pores is larger, and consequently, the free chloride content in the saturated solution in the pores increases when the total chloride content increases. For the same water-to-cement ratio, longer curing times correspond to a higher degree of maturity of the C-S-H gel (a higher surface area and higher tortuosity of pore structure), which means more bound chloride and lower diffusivity. Since the diffusivity of aggregates is usually lower than that of cement paste, the ratio of the effective diffusivity of concrete to the diffusivity of cement paste decreases with increasing volume fraction of aggregate.
5. The present models for chloride binding capacity and

diffusivity are incorporated in the chloride diffusion equation for saturated concrete. The equation is solved by a finite-difference method, and the predicted profiles of chloride penetration agree with test results quite well.

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