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A study of the effect of chloride binding on service life predictions

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Abstract

One of the major causes of deterioration of reinforced concrete structures is chloride-induced corrosion of the reinforcing steel. The magnitude of the damage is especially large in structures exposed to marine environments and de-icing salts. The capacity of the concrete cementitious system to bind chloride ions has an important effect on the rate of chloride ionic transport in concrete and on the corrosion initiation of the steel reinforcement. This paper reviews mathematical models used in the literature to describe chloride binding in concrete. The impact of the different binding relations on the time-dependent chloride penetration profiles is investigated by solving the chloride mass conservation statement with a finite-difference approach. Results are presented for a concrete structure subjected to two different exposure conditions: submerged in seawater and exposed to de-icing salts. The implication of accounting for chloride binding in service life estimations is discussed. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Chloride-induced corrosion of steel bars in reinforced concrete exposed to marine environments and de-icing salts has become one of the major causes of deterioration in many important facilities made of reinforced concrete (e.g., bridge decks and parking garages). Corrosion damage in these structures is usually manifested by rust-staining of the surface and by cracking and spalling of the concrete cover due to the expansion of the corrosion products. It can also lead to future structural distress due to the loss of the reinforcing steel cross-sectional area as well as loss of bond along the steel–concrete interface.

In general, the highly alkaline medium provided by the cement matrix in concrete maintains the reinforcing steel in a passive state, where the corrosion rate is insignificantly low due to the formation of a layer of iron oxide on the steel. However, a localized breakdown of the passivating layer occurs when a sufficient amount of chlorides reach the reinforcing bars, and the corrosion process is then initiated. Chlorides in concrete can be either dissolved in the pore solution (free chlorides), or chemically and physically bound to the cement hydrates and their surfaces (bound chlorides). Only the free chlorides dissolved in the pore solution are responsible for initiating the process of corrosion [1], since it is in this state that they continue to penetrate through the concrete cover.

The effect of chloride binding in concrete on the initiation of corrosion is twofold: (1) the rate of chloride ionic transport in concrete is reduced, since the amount of available mobile ions (free chlorides) is also reduced by the binding mechanisms; and (2) the reduction of free chlorides in concrete results in lower amounts of chlorides being accumulated at the reinforcing steel layer [2]. The objective of this paper is to review published chloride binding models and to discuss their impact on the calculated time-dependent chloride profiles. Although chloride penetration in concrete may occur as a result of several transport mechanisms (ionic diffusion, capillary sorption, permeation, dispersion, and wick action), the work presented here focuses on the effect of chloride binding on ionic diffusion under the assumption that the concrete cover is fully saturated. The effect of chloride binding on other transport mechanisms has not been investigated as much, though experimental studies on absorption of chloride contaminated water by concrete have shown that the chloride front moved into the concrete

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at a slightly lower rate than the water in which chlorides were dissolved [3], suggesting that chloride binding also affects the amount of chloride ions being transported by moisture flow.

2. Chloride diffusion

Provided that concrete is in a saturated state, chloride ions enter the concrete by ionic diffusion due to the existing concentration gradient between the exposed surface and the pore solution of the cement matrix (diffusion driving force). This process is often described by Fick's 1st law of diffusion, according to which, the rate of transfer of chloride ions J_c through a plane perpendicular to the direction of diffusion is proportional to the concentration gradient $\partial C_f/\partial x$ [4], i.e.,

$$Jc = -D_c \cdot \omega_e \cdot \frac{\partial C_f}{\partial x} = -\overline{D_c} \cdot \frac{\partial C_f}{\partial x} \quad [\mathrm{kg/(m^2 \cdot s)}] \qquad (1)$$

where J_c is the flux of chloride ions due to diffusion (kg/m^2·s), D_c is the effective diffusion coefficient when the concentration is expressed in kilograms per cubic meter of concrete (m^2/s), $\overline{D_c}$ is the effective diffusion coefficient when the concentration is expressed in kilograms per cubic meter of pore solution (m^2/s), ω_e is the evaporable water content (m^3 evaporable water/m^3 concrete), and C_f is the free chloride concentration (kg/m^3 of pore solution) at depth x (m). The negative sign in Eq. (1) indicates that diffusion occurs in the opposite direction to that of increasing chloride concentration. It is assumed here that the water in which chloride diffusion occurs is equal to ω_e [5,6] Establishing chloride mass conservation in saturated concrete results in:

$$\frac{\partial C_t}{\partial t} = -\frac{\partial J_c}{\partial x} \quad [\mathrm{kg/(m^3 \cdot s)}] \qquad (2)$$

where C_t is the total chloride concentration (kg/m^3 of concrete) and t is time (s). If Eq. (1) is substituted into Eq. (2), the equation governing the mechanism of chloride diffusion in concrete (Fick's 2nd law) is given by:

$$\frac{\partial C_t}{\partial t} = \frac{\partial}{\partial x}\left(D_c \cdot \omega_e \cdot \frac{\partial C_f}{\partial x}\right) \quad [\mathrm{kg/(m^3 \cdot s)}] \qquad (3)$$

Eq. (3) expresses the change of total chloride concentration with time ($\partial C_t/\partial t$) as a function of the spatial gradient of free chlorides ($\partial C_f/\partial x$).

The total, bound, and free chloride concentrations in concrete are related by [5,7]:

$$C_t = C_b + \omega_e C_f \quad [\mathrm{kg/m^3 \ of\ concrete}] \qquad (4)$$

where C_b is the concentration of bound chlorides (kg/m^3 of concrete). If chloride binding is disregarded (i.e., C_b=0), the solution of Eq. (3) can be readily obtained since C_t=$\omega_e C_f$. However, if binding of chloride ions in concrete is to be accounted for, Eq. (3) needs to be written in terms of the same chloride concentration. The binding properties of a specific cement composition are usually defined in the form of a binding relation (Fig. 1), with the amount of bound chlorides C_b expressed as a function of the amount of free chlorides C_f. To take into account chloride binding in the solution of Eq. (3), binding relationships have to be determined experimentally for each cementitious system under consideration.

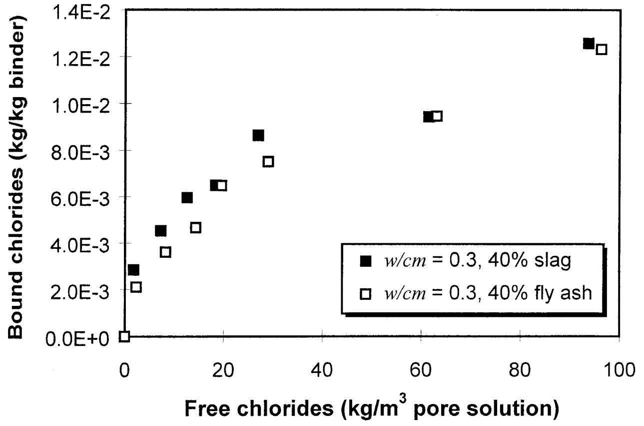

Fig. 1. Chloride binding isotherms obtained at the University of Toronto for two cement pastes with w/cm = 0.3 and 40% slag and fly ash replacement levels, respectively.

By applying mass conservation to Eq. (4) and substituting into Eq. (3), the following modified Fick's 2nd law equation results [6]:

$$\frac{\partial C_f}{\partial t} = \frac{\partial}{\partial x}\left(D_c^* \frac{\partial C_f}{\partial x}\right) \quad [\mathrm{kg/(m^3 \cdot s)}] \qquad (5)$$

with

$$D_c^* = \frac{D_c}{1 + \frac{1}{\omega_e}\frac{\partial C_b}{\partial C_f}} \quad [\mathrm{m^2/s}] \qquad (6)$$

where D_c* is the apparent diffusion coefficient (m^2/s) and $\partial C_b/\partial C_f$ is the "binding capacity" of the concrete binder (m^3 of pore solution/m^3 of concrete) as defined by Nilsson et al. [7]. The binding capacity of a specific cementitious system is given by the slope of the corresponding binding relation. Note that Eq. (5) is now written in terms of the free chloride concentration C_f. Once the binding relation that characterizes the specific concrete binder is known and the concentration of free chlorides is determined (by solving Eq. (5)), the total amount of chlorides in concrete is calculated from Eq. (4).

3. Chloride binding isotherms

Chloride binding isotherms describe the relationships between free and bound chlorides in concrete at a given temperature. They are unique to each cementitious system since they are influenced by the components making up that system, such as C_3A content, supplementary cementing materials, and pH of the pore solution. They are also influenced by the environmental conditions surrounding the system such as temperature.

3.1. Experimental data

The binding data illustrated in Fig. 1 were obtained by an experimental procedure developed by Tang and Nilsson [8]. This procedure is based on the concept of immersing paste or mortar specimens in a chloride solution until equilibrium is reached between the specimen pore solution and the external solution. It is then assumed that the chloride concentration in the pore solution (free chlorides concentration) is equal to the chloride concentration in the external solution. The amount of bound chlorides is estimated from the decrease in the chloride concentration of the external solution.

For the data shown in Fig. 1, two cement pastes with a water-to-cementitious material ratio (w/cm) of 0.3% and 40% slag and fly ash replacement levels, respectively, were tested. The mixing was done in a 3.8-l stainless-steel, high speed blender. The mixing procedure involved 1 min of mixing followed by 1 min of rest in order to scrape the inside surface of the blender, and additional 3 min of mixing. The mixing was done under vacuum conditions to minimize air bubbles within the paste. After mixing, the pastes were cast in sealed plastic cylinders (100 × 50 mm diameter) and then rotated for 24 h to prevent segregation. The sealed pastes were cured at 100% relative humidity for a 2-month period. At the end of the curing period, the pastes were demoulded, and the central portion was cut into approximately 3-mm-thick discs. The sliced samples were vacuum dried in a desiccator containing silica gel and soda lime for 3 days. They were then stored for a month in a glove box that was kept at 11% relative humidity by using a saturated LiCl solution. Soda lime was also used in the glove box to remove the carbon dioxide from the air inside it. After storage, 25-g samples were put into plastic bottles and placed under vacuum for about 2 h before being filled with NaCl solutions saturated with $Ca(OH)_2$. Seven NaCl concentrations were used in this study: 0.1, 0.3, 0.5, 0.7, 1.0, 2.0, and 3.0 M. The bottles were kept at 22°C until equilibrium was reached. The solutions were then tested for their chloride ion concentration by potentiometric titration using 0.01 $AgNO_3$. The bound chloride content was estimated using the Eq. (7):

$$C_\mathrm{b} = 35.453V(C_\mathrm{i} - C_\mathrm{e})/W_\mathrm{d} \quad [\text{mg/g of paste}] \tag{7}$$

where C_b is given in mg/g of sample, V is the volume of the solution (ml), C_i is the initial chloride concentration of the solution (mol/l), C_e is the chloride concentration of the solution at equilibrium (mol/l), and W_d is the mass of the dry sample (g). The chloride binding isotherms shown in Fig. 1 were obtained by plotting C_e vs. C_b for the seven NaCl concentrations.

3.2. Mathematical models

The following is a review of some of the theoretical curves used in the literature to describe chloride binding in concrete. The corresponding binding capacities and the resulting apparent diffusion coefficients as given by Eq. (6) are listed as well.

No binding [Eq. (8)]:

$$C_\mathrm{b} = 0 \qquad \frac{\partial C_\mathrm{b}}{\partial C_\mathrm{f}} = 0 \qquad D_\mathrm{c}^* = D_\mathrm{c} \tag{8}$$

Linear isotherm:

$$C_\mathrm{b} = \alpha C_\mathrm{f} \qquad \frac{\partial C_\mathrm{b}}{\partial C_\mathrm{f}} = \alpha \qquad D_\mathrm{c}^* = \frac{D_\mathrm{c}}{1 + \frac{\alpha}{\omega_\mathrm{e}}} \tag{9}$$

where α is the slope of the line. Although several experimental works have reported that the relationship between bound and free chlorides is non-linear [5,7–9] chloride binding is often assumed to be linear for modeling purposes [10]. A reason for this is that it simplifies the solution of Eq. (5), since the binding capacity is constant and does not depend on the level of free chloride ions. However, as pointed out by Nilsson et al. [2], a linear binding relationship oversimplifies the binding mechanism process. A linear relation underestimates the amount of bound chlorides at low free chloride concentrations, where the binding capacity has been observed to be non-constant with a high rate of change [11], whereas it overestimates the amount of bound chlorides at high free chloride concentrations (see Fig. 2 where the linear binding relation was forced through the origin and fit by the least-squares method). Yet, the margin of free chloride concentrations for which the fit is made has a significant impact on the quality of the fit. The binding capacity α increases as the fit is made for lower levels of free chlorides and a lower range of concentrations, as illustrated in Fig. 2. Tuutti [1] obtained linear relationships that fit very well his chloride binding data; however, he just reported values of free chloride concentrations lower than 20 kg/m^3.

Langmuir isotherm:

$$C_\mathrm{b} = \frac{\alpha C_\mathrm{f}}{1 + \beta C_\mathrm{f}} \qquad \frac{\alpha C_\mathrm{b}}{\alpha C_\mathrm{f}} = \frac{\alpha}{(1 + \beta C_\mathrm{f})^2} \tag{10}$$

$$D_\mathrm{c}^* = \frac{D_\mathrm{c}}{1 + \frac{\alpha}{\omega_\mathrm{e}(1 + \beta C_\mathrm{f})^2}}$$

where the binding constants α and β vary according to the concrete binder composition. Sergi et al. [5] obtained the values of α and β as 1.67 and 4.08, respectively, by linear regression analysis of data from OPC paste samples with w/c=0.5 (C_f and C_b were expressed by the authors as mol/l and mmol/g of cement, respectively). In spite of the fact that Sergi et al. [5] recognized the non-linear nature of the relationship, the authors concluded that a linear approximation (β=0) gives a good description of the phenomenon. Tang and Nilsson [8] have stated that the relationship between bound and free chlorides is best described by the Langmuir isotherm when the concentration level of chlorides in the pore solution is less than 1.773 kg/m^3. The slope of the Langmuir isotherm (binding capacity) tends to approach to zero as the concentration of free chlorides increases, suggesting that there is an upperbound in the amount of chlorides being bound (Fig. 2).

Freundlich isotherm:

$$C_{\mathrm{b}} = \alpha C_{\mathrm{f}}^{\beta} \qquad \frac{\partial C_{\mathrm{b}}}{\partial C_{\mathrm{f}}} = \alpha\beta C_{\mathrm{f}}^{\beta - t} \tag{11}$$

$$D_{\mathrm{c}}^{*} \; \frac{D_{\mathrm{c}}}{1 + \frac{1}{\omega_{\mathrm{e}}}\alpha\beta C_{\mathrm{f}}^{\beta - 1}}$$

Tang and Nilsson [8] found that this relationship works best for high free chloride concentrations (>0.355 kg/m^3 of pore solution). Their experimental results showed that concrete binders still exhibit a binding capacity at high concentrations of free chlorides, as opposed to what is suggested by the Langmuir relation. According to Tang and Nilsson [8], monolayer adsorption occurs when the free chloride concentration is very low (described by the Langmuir isotherm); however, a more complex adsorption phenomenon takes place at high levels of chloride concentration, where the amount of bound chlorides increases with the free chlorides concentration.

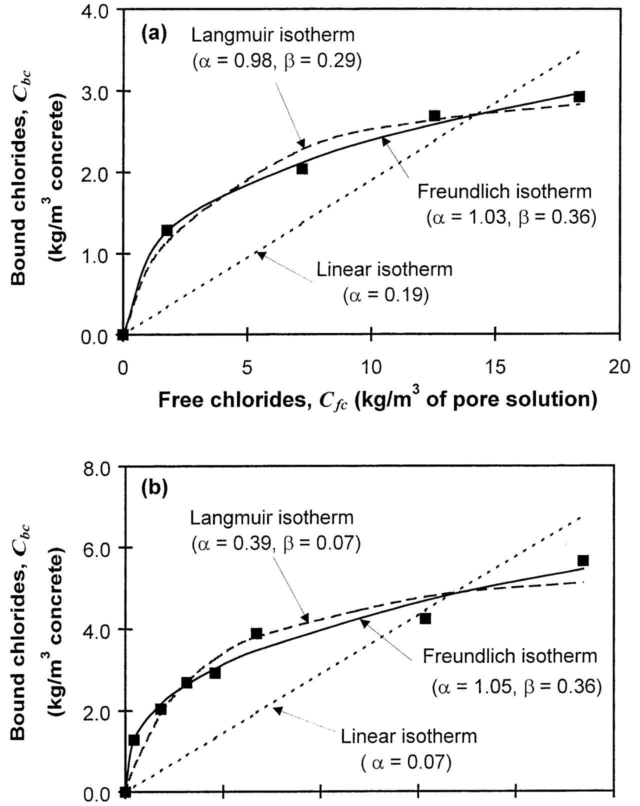

Fig. 2. Idealized binding isotherms for a concrete with 40% slag replacement level and w/cm = 0.3 according to the isotherm shown in Fig. 1 for two different exposure conditions: (a) C_{s} = 0.5 M and (b) C_{s} = 2.5 M. (It was assumed that ω_{e} = 8% and the binder content was 450 kg/m^3 of concrete.)

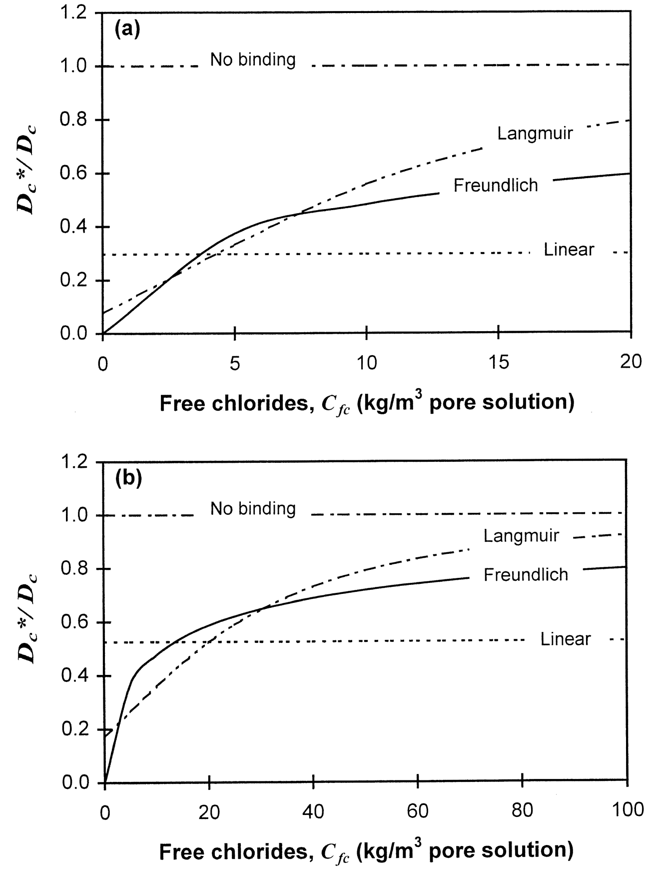

Fig. 3. The effect of chloride binding on the apparent diffusion coefficient for a concrete with 40% slag replacement level and w/cm = 0.3 according to the isotherms shown in Fig. 2 for two different exposure conditions: (a) C_{s} = 0.5 M and (b) C_{s} = 2.5 M.

Note that the relationships given by Eqs. (9)–(11) assume that equilibrium between free and bound chlorides is established instantaneously, and that perfectly reversible conditions apply. However, observations reported from field studies where the total concentration at the surface increased with time in spite of constant exposure conditions [12] suggest that chloride binding may actually be a transient process. Moreover, the change of the pore solution pH due to leaching of concrete hydroxyl ions is known to affect the chloride binding relationship. Thus, a proper representation of the chloride binding mechanism should also take this phenomenon into account. Attempts to incorporate the influence of pH in the numerical modeling of chloride binding and diffusion have already been carried out by Sergi et al. [5] and Tang and Nilsson [13].

The effect of chloride binding in Eq. (6) is to reduce the diffusivity of chloride ions in concrete by an amount that is representative of the binding capacity of the specific binder (see Fig. 3). In the case of ignoring binding or considering a linear binding isotherm, the apparent diffusion coefficient D_c* is constant as chlorides penetrate the concrete; however, when non-linearities are taken into account in the bound-free chloride relation, D_c* is allowed to vary through the concrete depth, which reflects the dependence of the chloride binding capacity of the concrete binder on the levels of chloride ions in the pore solution [7]. Note that when the above binding isotherms are fitted to the data of Fig. 1 up to a range of free chlorides of 0.5 M, the binding capacity of the linear relationship is higher than the non-linear ones for chloride concentrations higher than 5 kg/m^3 of pore solution (Fig. 3a). When the data is fitted up to 2.5 M, this value is increased to 20 kg/m^3 of pore solution (Fig. 3b).

4. Numerical model

The governing partial differential equation given by Eq. (5) cannot be solved without the use of numerical methods because of the dependency of D_c* on C_f for non-linear binding isotherms. Eq. (5) was solved here numerically in space as a boundary-value problem and in time as an initial-value problem by means of a one-dimensional finite-difference formulation (Crank–Nicolson scheme). The purpose in the development of a chloride penetration computer model was to study the influence of different chloride binding isotherms on the calculated chloride concentration profiles with respect to time.

The set of simultaneous equations that results from applying the finite-difference method to Eq. (5) was solved in time steps until a specified chloride threshold was reached at the reinforcing steel layer. To ease the computation of the solution, it was assumed that the apparent diffusion coefficient D_c* was dependent upon the level of the free chloride concentration at the previous time step instead of that at the current time step. This resulted in an error in D_c* of approximately 10% for very low free chloride concentrations, since the binding capacity of non-linear relations is higher and more sensitive to changes at low ranges of free chlorides (Fig. 3). As the concentration of chlorides in the pore solution increased, the error in D_c* was less than 5%. The time step used was 1 day.

The initial and boundary conditions used for the numerical analyses were expressed as [Eq. (12)]:

$$\begin{aligned} &\text{For } t = 0: \quad && C_f = C_o \quad \text{at } x > 0 \\ &\text{For } t \geq 0: \quad && C_f = C_s \quad \text{at } x = 0 \\ & && C_f = C_o \quad \text{at } x = L \end{aligned} \tag{12}$$

where C_o is the concentration of chlorides present in the pore solution before the concrete is exposed to a salt solution (kg/m^3 of pore solution), C_s is the chloride concentration of the salt solution in contact with the outer surface (kg/m^3 of solution), and L is the thickness of the member. It was assumed here that the thickness of the concrete member was much larger than the penetration depth. A value of L=200 mm was used in the numerical analyses.

5. Analysis results

Numerical analyses were performed with the computer model in order to study the effect of the binding isotherm nature on the chloride concentration profiles. Three different cases were analyzed: one in which binding was neglected; a second one in which a linear relationship between bound and free chlorides was assumed; and, a third one in which non-linear binding was taken into account. The input parameters required to perform the numerical analyses were evaluated from the chloride binding data illustrated in Fig. 2, which also shows the best fits of the various theoretical relations reviewed in Section 3.2 for two different ranges of chloride concentrations (0.5 and 2.5 M, respectively). The respective binding constants were obtained by applying the least-squares method to the given data. Note that these values depend on the units used for C_f and C_b (in this case kg/m^3 of pore solution and kg/m^3 of concrete, respectively). The Freundlich isotherm was used to describe non-linear binding in the numerical simulations, since the data fitting gave a higher coefficient of determination than the Langmuir relation.

Since the chloride binding data in Fig. 2 were obtained from cement paste samples, it was assumed that the concrete evaporable water content ω_e was 8%, the binder content was 450 kg/m^3 of concrete, and the effective diffusion coefficient D_c was 1.0×10^{-12} m^2/s at 120 days (a value in the range for concretes made with the above cementitious system at later ages [14]). It was further assumed that all chlorides in the concrete came from external sources (i.e., C_o=0). Two different surface conditions were considered in the calculations: 0.5 and 2.5 M NaCl concentration solutions. The former condition simulates complete submersion in sea water, whereas the latter simulates conditions more characteristic of marine structures in the splash zone or bridge decks exposed to de-icing salts. It is assumed in the latter case that, although water evaporation at the concrete surface occurs increasing the concentration of chloride ions in the pore solution, the concrete pores at the surface are still filled with solution (assumption necessary to apply diffusion as the main transport mechanism).

Calculated free and total chloride profiles are respectively plotted in Figs. 4 and 5 for C_s=0.5 M and in Figs. 6 and 7 for C_s=2.5 M. The chloride concentration profiles are shown after an exposure period of 6 months, 5 years, and 50 years for the 0.5 M surface condition, and after an exposure period of 6 months, 5 years, and 30 years for the 2.5 M surface condition. If non-linear binding is accounted for, the

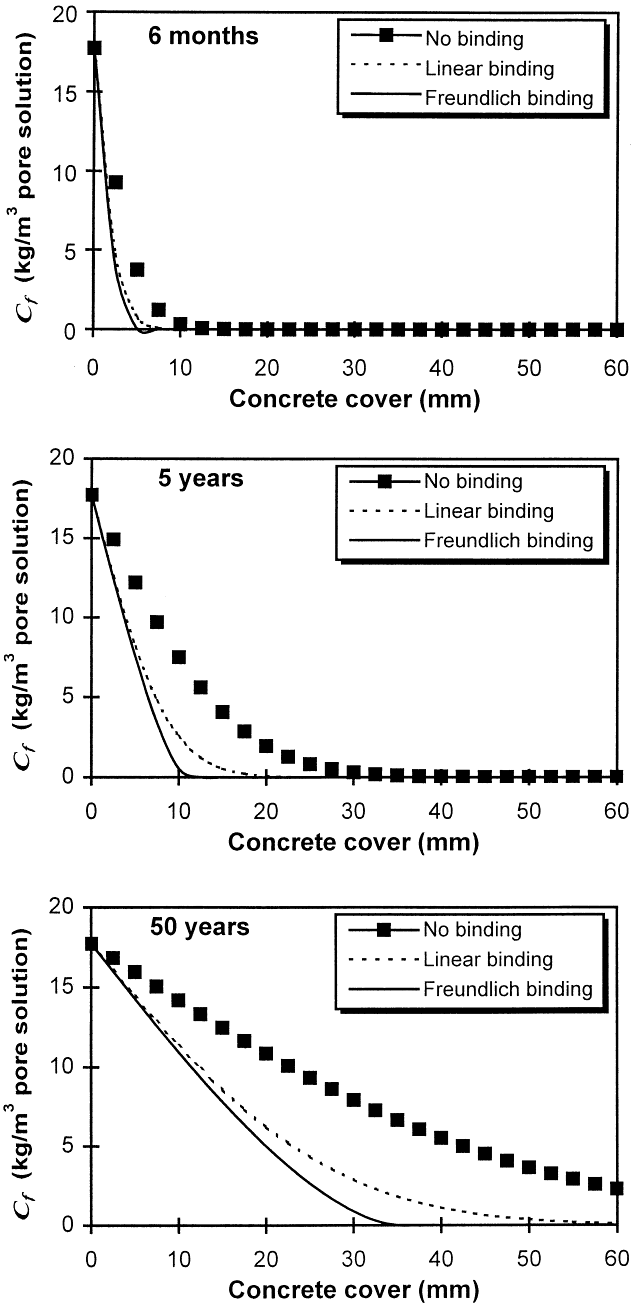

Fig. 4. Free chloride concentration profiles at (a) 6 months, (b) 5 years, and (c) 50 years for 0.5 M exposure conditions.

level of concentration of free chlorides at a given depth is lower than if a linear relation or no binding at all are assumed for both exposure conditions. This difference becomes more significant at greater concrete depths as the time of exposure increases (Figs. 4c and 6c). It is worth noting that, even though the reduction in D_c* is higher for the linear relationship compared to the Freundlich one for high levels of chloride concentration (see Fig. 3), the free chloride profiles are lower for the Freundlich binding isotherm in all cases. This implies that the effect of introducing chloride binding in the diffusion problem becomes more significant at lower chloride concentrations, at which the reduction in D_c* is more pronounced for the Freundlich binding relationship.

The difference in shape of the total chloride profiles corresponding to no binding, linear binding, and non-linear binding results from the dependency of the respective binding capacities on the level of free chloride ions. This difference is more significant at low chloride concentrations, where the binding capacity of the non-linear relation is higher and more sensitive to the change in concentration of

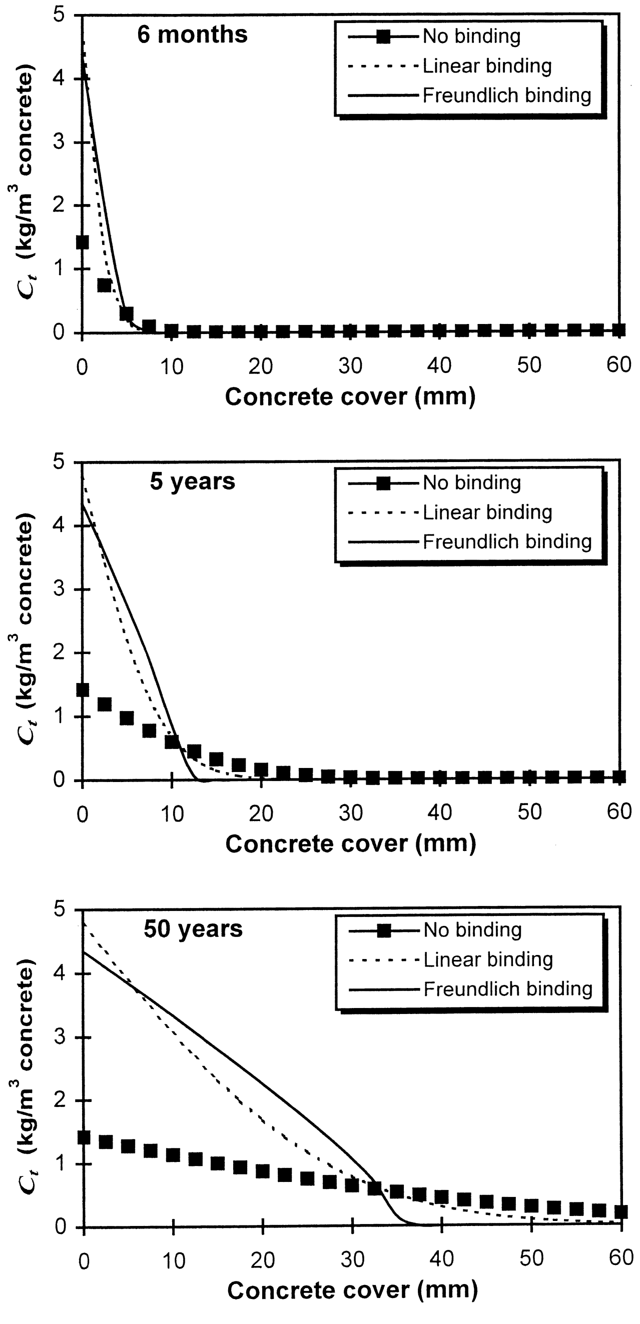

Fig. 5. Total chloride concentration profiles at (a) 6 months, (b) 5 years, and (c) 50 years for 0.5 M exposure conditions.

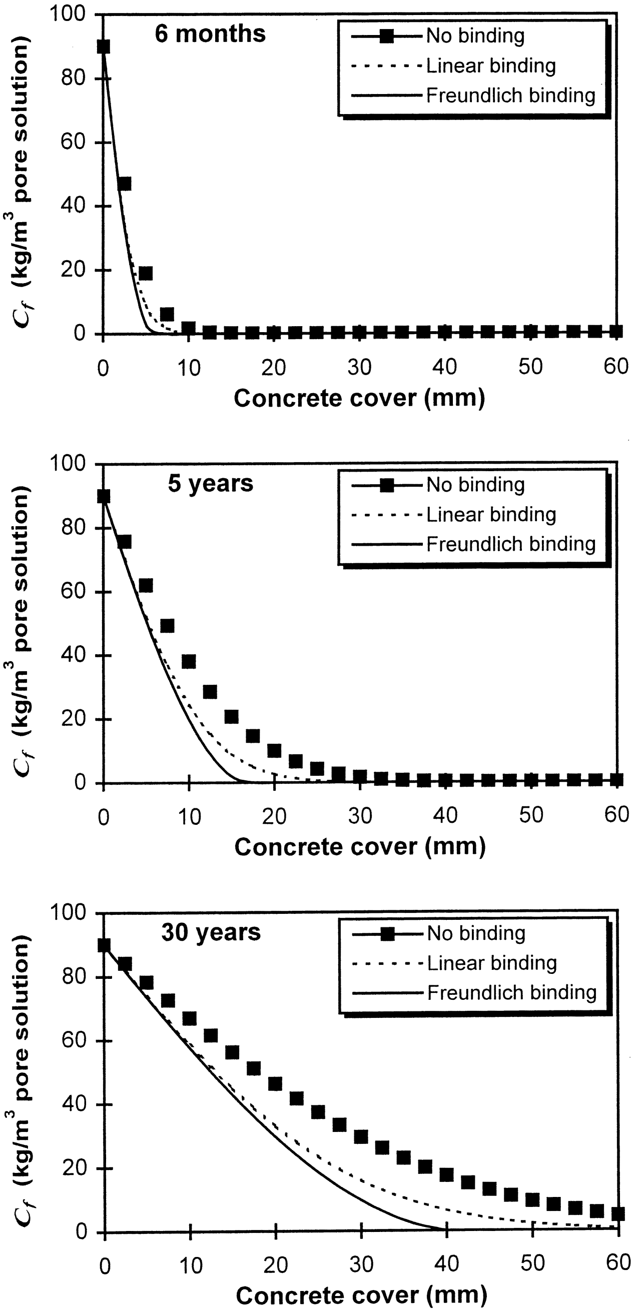

Fig. 6. Free chloride concentration profiles at (a) 6 months, (b) 5 years, and (c) 30 years for 2.5 M exposure conditions.

free chlorides (Fig. 3). Note that different values of C_t at the surface result for the different binding relationships, even though the external solution C_s is the same for the three cases (Figs. 5 and 7). For both cases where the external solutions are 0.5 M (17.7 kg/m^3) and 2.5 M (90 kg/m^3), respectively, the linear relation results in a higher amount of bound chlorides at the surface compared to that of the Freundlich relation. The reason for this is the higher binding capacity of linear isotherms at high free chloride concentration levels (see Fig. 2).

Up to a certain depth, the profiles of C_t for non-linear binding are higher than the linear ones, which in turn are higher than the ones without binding. This emphasizes the importance of defining the nature of the threshold concentration, i.e., in terms of free or total chlorides. It seems to be more appropriate to define the threshold value in terms of free chlorides, since these are the ones that penetrate through the concrete cover and initiate corrosion. The profiles in terms of total chlorides as shown in Figs. 5 and 7 can be misleading in this respect. Higher profiles here mean more chloride ions being bound along the diffusion

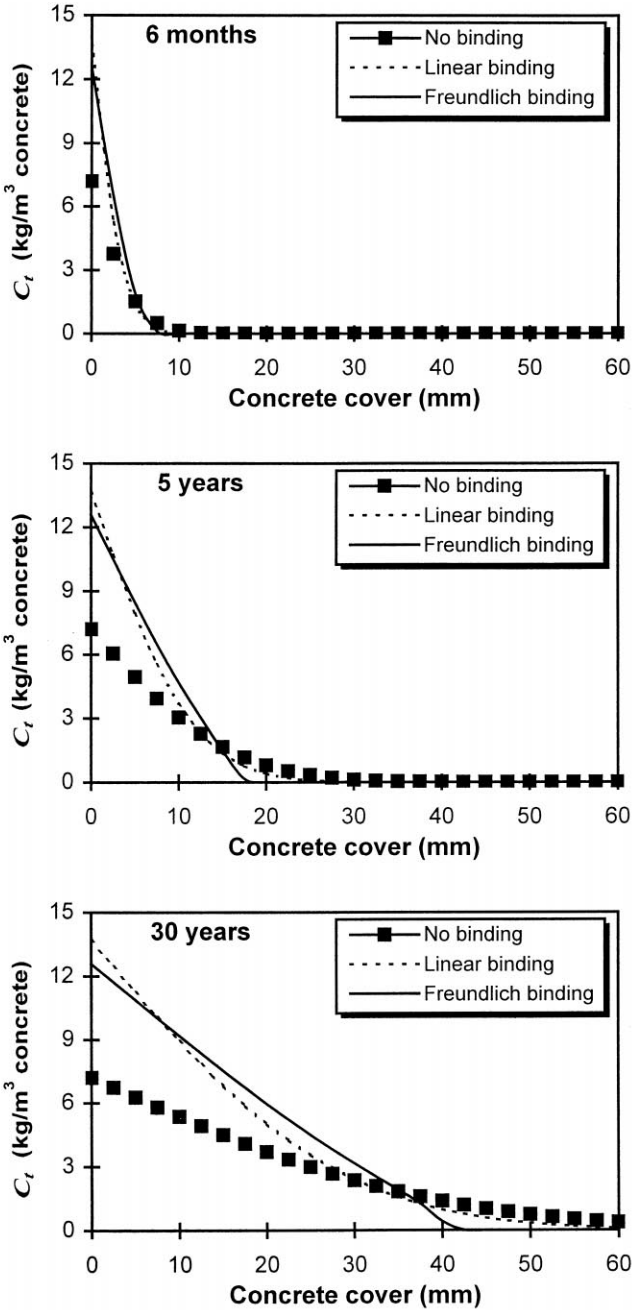

Fig. 7. Total chloride concentration profiles at (a) 6 months, (b) 5 years, and (c) 30 years for 2.5 M exposure conditions.

path. However, it is well known that weakly bound chlorides can be released into the pore solution and present risk for corrosion as well [15]. Yet, if a proper mathematical representation of the chloride binding mechanism accounts for the adsorption/desorption of chlorides in the calculations, the potential for releasing bound chlorides is included in the results.

Fig. 8 shows the resulting service life estimates for the different binding isotherms shown in Fig. 2 and different concrete covers (40 and 60 mm) for the two different exposure conditions (0.5 and 2.5 M, respectively). Service life predictions were obtained by assuming that the service life of a reinforced concrete structure subjected to chloride ingress corresponds to the period until reinforcing steel depassivation. The free chloride threshold concentration used was 0.09% by mass of cementitious material, a lowerbound reported in Glass and Buenfeld [15]. The 0.09% by mass corresponds to 5.0 kg/m^3 of pore solution based on the assumption of a 450 kg/m^3 binder content and an evaporable water content of 8% by volume. The nature of the binding relation has a significant effect on the results; these show a 238% and 352% increase in time to steel depassivation for C_s=0.5 M, and a 93% and 200% increase for C_s=2.5 M when linear and Freundlich binding are considered, respectively. The relative increase in time to corrosion initiation is less pronounced for the higher surface concentration case, since at high levels of chloride concentrations the ratio of bound-to-free chlorides is smaller. While these service life estimates can serve to compare the performance of different cementitious systems with known binding properties and subjected to the same conditions, the prediction of the time to corrosion of a specific concrete structure should also take into account the simultaneous effect of other critical factors (e.g., capillary absorption, diffusivity time dependency, temperature, etc.)

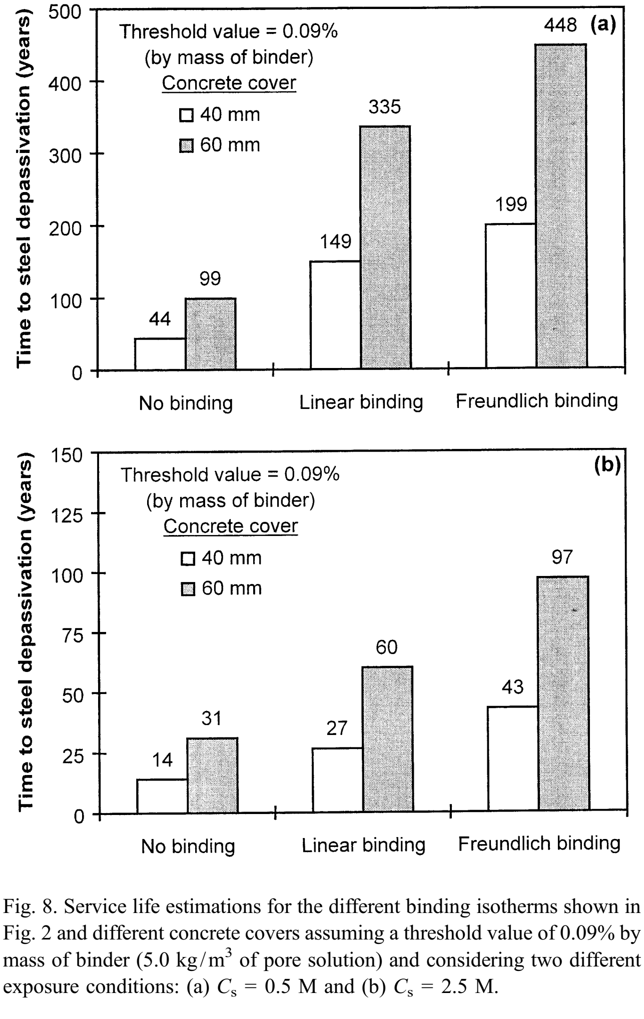

Fig. 8. Service life estimations for the different binding isotherms shown in Fig. 2 and different concrete covers assuming a threshold value of 0.09% by mass of binder (5.0 kg/m^3 of pore solution) and considering two different exposure conditions: (a) C_s = 0.5 M and (b) C_s = 2.5 M.

6. Conclusions

A review of published mathematical models used to describe chloride binding in concrete has been presented. The effect of these models on the time-dependent chloride concentration profiles was investigated by means of a finite-difference solution to the chloride diffusion equation in concrete given two different exposure conditions. From the numerical analysis, it was found that reducing the concrete chloride diffusivity along the diffusion path by an amount representative of the binding capacity of the cementitious system resulted in lower free chloride penetration depths, particularly as the time of exposure increased. The margin of free chloride concentrations (i.e., the specified exposure conditions) for which the fit of the presented models to the reported binding data was made affected the values of the obtained binding constants and, therefore, the computed chloride profiles. Although the quality of the fitting affected mainly the binding constant corresponding to the linear relation, the impact of introducing non-linear binding in the numerical calculations was particularly significant at low levels of free chlorides for the chloride binding data used in this study, regardless of specified conditions at the surface. Although the linear relation presented a better fitting the lower the exposure condition was, it was not able to capture the highly non-linear nature at this range of the reported chloride binding data. The nature of the binding relationship assumed for modeling purposes also had a significant impact on service life predictions.

From the results of the study, it was observed how significantly dependent the calculated chloride profiles are on the assumed binding relationship used in the analysis. Consequently, the understanding of the binding properties of a given cementitious system and the use of the appropriate binding relationship in numerical calculations enables the engineer to better estimate chloride penetration depths and, therefore, depassivation time of reinforcing steel.

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