



## PHYSICOCHEMICAL PROCESSES AND MATHEMATICAL MODELING OF CONCRETE CHLORINATION

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**Abstract**—Corrosion of steel bars in concrete may start when the concentration of free chlorine ions in the liquid phase of the pores exceeds a certain threshold level causing depassivation of the bars. The physicochemical processes of diffusion of  $\text{Cl}^-$  in the aqueous phase of the pores, their adsorption and binding in the solid phase of concrete and their desorption therefrom are described by a nonlinear partial differential equation for the concentration of  $\text{Cl}^-$  in the aqueous phase, from which that of  $\text{Cl}^-$  bound in the solid phase can be computed algebraically. A simple yet accurate enough approximate analytical solution is also proposed, based on the assumption of the formation of a “chlorination front” where all the absorption and binding of  $\text{Cl}^-$  takes place, and beyond which no effects of the ingress of  $\text{Cl}^-$  from the environment are felt. Model parameters are identified through fitting to experimental results. Parametric studies allow identification of the relative importance of the various geometric, physicochemical and environmental exposure parameters.

### 1. INTRODUCTION

Concrete carbonation and chlorination are the two main physicochemical processes which limit the useful lifetime of reinforced concrete structures. Steel bars in reinforced concrete are protected from corrosion in the presence of moisture and oxygen by a microscopic oxide layer which forms on their surface due to the high alkalinity ( $\text{pH} \approx 13$ ) of the surrounding concrete. Protection from corrosion ends if this passive layer disappears due to “carbonation” of the surrounding concrete (i.e. the reaction of its  $\text{Ca}(\text{OH})_2$  with atmospheric  $\text{CO}_2$  and the subsequent drop of the pH value of the pore water) or due to reaction with free chlorine ions dissolved in the pore water. Depassivation of the steel bars takes place when the concentration of chlorine ions in the vicinity of the bars exceeds a threshold value, of the order of 0.05% by weight in noncarbonated concrete. This threshold level refers to the concentration of free chlorine ions and not to the total of free ions plus those bound in the solid skeleton of the concrete.

Contributions of practical or experimental character regarding the effects of chlorides and carbonation on corrosion of steel in concrete abound in the literature (e.g. Tuutti, 1982; ACI Committee 222, 1985; Morinaga, 1988; Richardson, 1988; CEB, 1989; Bijen, 1989). Despite the wealth of practical, yet qualitative and empirical, information and of relevant measurements in the laboratory or in real structures, efforts in the direction of modeling the phenomena and

the physicochemical processes are very limited. The present authors were the first to develop and experimentally verify a fundamental and comprehensive reaction engineering model of the processes leading to carbonation of concrete (Papadakis *et al.*, 1989, 1991a–c, 1992a, b). Regarding the effect of chlorides, Pereira and Hegedus (1984) were the first and the only ones to identify and model chloride diffusion and reaction in fully saturated concrete as a Langmuirian equilibrium process coupled with Fickian diffusion. In the present work, the pioneering modeling effort of Pereira and Hegedus is generalized and extended to more general conditions and is offered alternative simpler, yet equally accurate, numerical and analytical solutions. Parametric studies are then performed regarding the effect of various parameters and exposure conditions on the evolution of the chloride content in concrete.

### 2. PHYSICOCHEMICAL PROCESSES

#### 2.1. Sources of chlorides in concrete

Concrete is a porous material. Its solid skeleton consists of gravel and sand, bound together by the hardened cement paste. Its pores are partly or completely filled with water. The degree of saturation of the pores depends on their diameter and on the relative humidity of the environment.

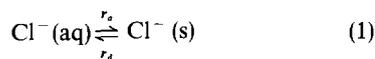
The source of chlorides in concrete may be internal or external. In the former and less common case, chlorides are present in the concrete from the very beginning. This is the case if chloride-containing admixtures are used in the concrete mix (e.g.  $\text{CaCl}_2$  is a main constituent of many admixtures added to accelerate the setting and hardening of concrete), or if

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seawater or beach aggregates are used in the concrete construction in coastal or marine regions away from supplies of nonsaline materials. In most cases of reinforcement corrosion due to chlorides, the source of chlorides is external. The use of de-icing salts in roads and highways during the winter is widespread in cold climates. Chlorides in these salts, dissolved in water, find easily their way into the concrete of bridge decks and abutments, into that of parking garages, etc. In marine environments, concrete is in contact with seawater, continuously in the submerged parts or periodically in the tidal and splash zones. In coastal areas, air and mist blown inland from the sea are laden with salts. Chlorides that reach the concrete surface in this or in the other way, enter the pore system either by diffusion in stationary pore water or by capillary suction of the surface water in which they are dissolved, or by a combination of both transport mechanisms.

## 2.2. Adsorption–reaction of chlorides in the solid phase of cement paste

Data in the literature (Rosenberg, 1964; Page and Vennesland, 1983; Pereira and Hegedus, 1984) suggest that binding of chloride ions in hardened cement paste is a reversible process tending to equilibrium. Chloride ions are adsorbed by calcium silicate hydrate (CSH) and by the other constituents of hardened cement paste, hydrated or not. They also chemically react with the  $C_3A$  and  $C_4AF$  constituents of cement ( $3CaO \cdot Al_2O_3$  and  $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ , respectively) and with the products of their hydration, producing the so-called Friedel's salt. So through these adsorption–reaction processes dissolved chloride ions,  $Cl^-$  (aq), are adsorbed chemically or physically in the solid phase of the cement paste as  $Cl^-$  (s). In turn some of the adsorbed  $Cl^-$  (s) is desorbed and the process tends to equilibrium between  $Cl^-$  (aq) and  $Cl^-$  (s). Denoting the rate of  $Cl^-$  (aq) adsorption in the solid phase by  $r_a$  and that of  $Cl^-$  (s) desorption in the aqueous phase by  $r_d$ , this reversible process is described by



As proposed and experimentally verified in fully saturated concrete by Pereira and Hegedus (1984), the adsorption of the  $Cl^-$  (aq) is a Langmuir process. The rate  $r_a$  can be taken as:

$$r_a = k_a \varepsilon f [Cl^- (aq)] ([Cl^- (s)]_{sat} - [Cl^- (s)]) \quad (2)$$

in which the parameters are defined in the Notation section. The desorption rate and the net rate of binding of  $Cl^-$  in the concrete,  $r$ , are given by

$$r_d = k_d [Cl^- (s)] \quad (3)$$

$$r \equiv r_a - r_d = k_a \varepsilon f [Cl^- (aq)] ([Cl^- (s)]_{sat} - [Cl^- (s)]) - \frac{k_d}{K_{eq}} [Cl^- (s)]. \quad (4)$$

## 2.3. Diffusion of chlorides in the aqueous phase of the pores

Chloride ions dissolved in the aqueous phase of the pores can be considered to diffuse in pore water according to Fick's law. The effective diffusivity coefficient of  $Cl^-$  (aq) in concrete,  $D_{e,Cl^-}$  ( $m^2/s$ ), depends on the molar diffusivity of  $Cl^-$  in water, on the porosity  $\varepsilon$ , the pore size distribution and the pore tortuosity of concrete and on the degree of pore saturation and the distribution of the pore water in the pores. In addition, the amount and the distribution of water in the concrete pores may change in time, due to the variation of the external humidity conditions. Mass transport and adsorption–desorption of pore water introduce additional transport mechanisms for  $Cl^-$  (aq). For practically constant pore water distribution, though, only diffusion of  $Cl^-$  (aq) takes place.

## 3. MATHEMATICAL MODELING

### 3.1. Generalized mathematical model

The mass-balance equations of  $Cl^-$  (aq) and  $Cl^-$  (s) are expressed as:

$$\frac{\partial (\varepsilon f [Cl^- (aq)])}{\partial t} = \nabla^2 (D_{e,Cl^-} [Cl^- (aq)]) - r \quad (5)$$

$$\frac{\partial [Cl^- (s)]}{\partial t} = r. \quad (6)$$

If the hydration of cement in practically complete and the amount and distribution of pore water is constant in space and time, then  $\varepsilon$ ,  $f$  and  $D_{e,Cl^-}$  are constant and can be taken out of the differential operators in eq. (5).

Equations (4)–(6), along with the appropriate initial and boundary conditions, constitute the mathematical model of the chloride adsorption–reaction–diffusion process in concrete with constant pore water distribution. These equations are essentially identical to those proposed by Pereira and Hegedus (1984) for the description of the diffusion–reaction–equilibrium process in fully saturated concrete ( $f = 1$ ), as a Langmuir process coupled with Fickian diffusion.

At steady-state the derivatives in eqs (5) and (6) and the rate,  $r$ , in eqs (4)–(6) vanish, resulting in the following (inversely linear) relation between the steady-state concentrations:

$$\frac{1}{[Cl^- (s)]_{\infty}} = \frac{1}{[Cl^- (s)]_{sat}} + \frac{1}{K_{eq} \varepsilon f [Cl^- (s)]_{sat}} \cdot \frac{1}{[Cl^- (aq)]_{\infty}}. \quad (7)$$

Equation (7) allows experimental determination of the parameters  $[Cl^- (s)]_{sat}$  and  $K_{eq}$  for known  $\varepsilon$  and  $f$ , through linear regression on measurements of pairs of values of steady-state concentrations  $[Cl^- (aq)]_{\infty}$  and  $[Cl^- (s)]_{\infty}$  taken on the same material for different initial  $Cl^-$  concentrations. This approach has been followed by Pereira and Hegedus (1984) and also herein for the determination of  $K_{eq}$  and  $[Cl^- (s)]_{sat}$ .

### 3.2. Solution of the differential equations

3.2.1. *Initial value problem: internal source of chlorides.* It is rather uncommon in good concrete construction practice to have the chlorides in the concrete from the very beginning. However, this initial value problem is also of interest because it lends itself to experimental measurement of  $k_a$ ,  $K_{eq}$ , and  $[Cl^- (s)]_{sat}$  as a function of concrete composition.

In the presence of uniform initial concentrations of chloride ions in the aqueous and/or the solid phase of concrete,  $[Cl^- (aq)]_{in}$  and  $[Cl^- (s)]_{in}$ , respectively, the initial conditions of the problem are:

$$I.C. \ t = 0 \quad [Cl^- (aq)] = [Cl^- (aq)]_{in},$$

$$[Cl^- (s)] = [Cl^- (s)]_{in}. \quad (8)$$

In eq. (5) the differential term with respect to the space variables is zero and eqs (4)–(6) are solved as a system of differential equations with respect to  $t$ . However, in early age concrete,  $\varepsilon$  and  $f$  cannot be taken as constant and the system of equations is solved only numerically. The variation of  $\varepsilon$  with time can be determined from the evolution of cement hydration after casting (Papadakis *et al.*, 1991a).

3.2.2. *Boundary value problem: external source of chlorides.* The source of chlorides is typically external. Then chlorides enter the concrete from the surface, through the aqueous phase of the pores. For constant-in-time boundary conditions, the initial conditions of eqs (8) are supplemented with

$$B.C. (1) \quad [Cl^- (aq)] = [Cl^- (aq)]_0 \quad (9)$$

over the part of the surface which is the (constant) source of chlorides, and

$$B.C. (2) \quad \partial[Cl^- (aq)]/\partial n = 0 \quad (10)$$

over the rest of the surface or at a plane of symmetry. The derivative in eq. (10) is in the direction of the normal to the external surface or to the plane of symmetry.

3.2.3. *Nondimensionalization and simplification.* Important conclusions about the effect of various parameters and possible simplifications can be reached if the variables and parameters entering the differential equations are made dimensionless as follows:

$$\lambda = \frac{[Cl^- (aq)]}{[Cl^- (aq)]_0} \quad \sigma = \frac{[Cl^- (s)]}{[Cl^- (s)]_{sat}} \quad (11)$$

$$z = \frac{x}{L} \quad \tau = \frac{D_{e,Cl^-}}{\varepsilon f L^2} t.$$

In eq. (11)  $[Cl^- (aq)]_0$  is a characteristic concentration (e.g. a given boundary value at the surface) and  $L$  a characteristic length of the problem, normalizing all coordinate variables  $x$ ,  $y$  or  $z$ . In the simplest and rather common case of a one-dimensional slab geometry,  $L$  can be taken as half the total thickness of the slab.

The net adsorption rate of  $Cl^-$  is also made dimensionless as:

$$\xi = \frac{r}{r_{max}} = \lambda (1 - \sigma) - \frac{\sigma}{\alpha} \quad (12)$$

in which

$$r_{max} = k_a \varepsilon f [Cl^- (aq)]_0 [Cl^- (s)]_{sat} \quad (13)$$

and

$$\alpha = \varepsilon f K_{eq} [Cl^- (aq)]_0.$$

The nondimensionalization yields the following nondimensional groups of variables:

$$\beta = \frac{[Cl^- (s)]_{sat}}{\varepsilon f [Cl^- (aq)]_0} \quad \Phi^2 = \frac{r_{max} L^2}{[Cl^- (aq)]_0 D_{e,Cl^-}}. \quad (14)$$

Parameter  $\beta$  is a measure of the maximum possible concentration of  $Cl^- (s)$  in concrete relative to the characteristic concentration of  $Cl^- (aq)$  in the aqueous phase. The Thiele modulus  $\Phi$  provides a measure of the characteristic time for  $Cl^-$  diffusion relative to that required for  $Cl^-$  adsorption–reaction.

The differential equations in terms of the non-dimensional variables and parameters are:

$$\frac{\partial \lambda}{\partial \tau} = \frac{\partial^2 \lambda}{\partial z^2} - \Phi^2 \xi \quad (15)$$

$$\beta \frac{\partial \sigma}{\partial \tau} = \Phi^2 \xi \quad (16)$$

and the corresponding initial conditions:

$$\text{for } \tau = 0; \lambda = \lambda_{in} \text{ and } \sigma = \sigma_{in}. \quad (17)$$

For a slab of thickness  $2L$  and simultaneous ingress of chlorides from both surfaces, the dimensionless boundary conditions are:

$$\text{for } z = 0: \lambda = 1 \text{ and for } z = 1: \partial \lambda / \partial z = 0. \quad (18)$$

For typical values of the parameters,  $\Phi^2$  assumes values several orders of magnitude greater than unity, whereas  $\partial \lambda / \partial \tau$  and  $\partial^2 \lambda / \partial z^2$  in eq. (15) are of the order of magnitude one. Then  $\Phi^2 \xi$  in this equation should also be of the same order, which implies that  $\xi$  must be much less than unity, i.e. practically zero. For  $\xi \approx 0$  eq. (12) yields

$$\sigma = \alpha \lambda / (1 + \alpha \lambda). \quad (19)$$

Substituting for  $\sigma$  from eq. (19) into eq. (16) and eliminating  $\Phi^2 \xi$  from eqs (15) and (16) yields a single partial differential equation, eq. (20) below, and an algebraic one, eq. (19) above, instead for a system of partial differential equations:

$$\frac{\partial \lambda}{\partial \tau} = \frac{(1 + \alpha \lambda)^2}{\alpha \beta + (1 + \alpha \lambda)^2} \frac{\partial^2 \lambda}{\partial z^2}. \quad (20)$$

The physical meaning of the simplification is that adsorption–reaction of  $Cl^- (aq)$  takes place almost instantaneously in comparison to chloride diffusion in the aqueous phase of the pores. Accordingly, the

adsorption rate constant  $k_a$  does not appear in the simplified model. A much shorter integration time-step and two to three orders of magnitude more CPU time are required for the solution of the full set of equations, eqs (4)–(6), than for the simplified version, eqs (19) and (20).

**3.2.4. Approximate analytical solution.** Experimental measurements of the total concentration of  $\text{Cl}^-$  in concrete  $[\text{Cl}(\text{s})] + \epsilon f [\text{Cl}^-(\text{aq})]$  and/or of that in the liquid phase alone  $[\text{Cl}^-(\text{aq})]$  as well as the results of numerical solutions of the type described above suggest that in the one-dimensional boundary value problem of chloride diffusion–reaction, the concentration  $\lambda$  decreases almost linearly with distance  $z$  from the surface. Only at large depths, where the exact value of  $\lambda$  is small and close to zero, there is strong deviation of the dependence of  $\lambda$  on  $z$  from linearity. The linear dependence is described by

$$\lambda = 1 - \frac{z}{z_{\text{Cl}}} \quad \text{for } 0 \leq z \leq z_{\text{Cl}}. \quad (21a)$$

$$\lambda = 0 \quad \text{for } z \geq z_{\text{Cl}} \quad (21b)$$

in which  $z_{\text{Cl}}$  is the normalized depth where the linear approximation of the actual distribution of  $\lambda$  intersects the  $z$ -axis.

Equation (21) implies the existence of a sharp “front” at depth  $z_{\text{Cl}}$  from the surface, separating a region where diffusion and adsorption–reaction of  $\text{Cl}^-$  have taken place from one in which it has not started yet. Behind, as well as beyond the front, we have in this approximation  $\partial^2 \lambda / \partial z^2 = 0$  and  $\Phi^2 \xi = 0$ . Right at the front both these terms should assume infinitely large values, satisfying eq. (15) with  $\partial \lambda / \partial \tau = 0$  and in view of eq. (16):

$$\frac{\partial^2 \lambda}{\partial z^2} = \beta \frac{\partial \sigma}{\partial \tau} \quad (22)$$

To determine  $z_{\text{Cl}}$ , both sides of eq. (22) are multiplied by  $dz_{\text{Cl}}$  and integrated from  $z = z_{\text{Cl}}^-$  to  $z = z_{\text{Cl}}^+$ , yielding

$$\left. \frac{d\lambda}{dz} \right|_{z=z_{\text{Cl}}^+} - \left. \frac{d\lambda}{dz} \right|_{z=z_{\text{Cl}}^-} = \beta \left( \sigma \frac{dz_{\text{Cl}}}{d\tau} \right)_{z=z_{\text{Cl}}^+} - \beta \left( \sigma \frac{dz_{\text{Cl}}}{d\tau} \right)_{z=z_{\text{Cl}}^-}. \quad (23)$$

Due to eq. (21), the two derivatives on the left-hand side (LHS) of eq. (23) are equal to zero and  $-1/z_{\text{Cl}}$ , respectively. So, the LHS of the equation equals  $1/z_{\text{Cl}}$ . For the right-hand side (RHS) to be also nonzero, the value of  $\sigma$  should be discontinuous at the “front”. At  $z = z_{\text{Cl}}^+$ ,  $\sigma$  is zero, as it has been considered that diffusion and reaction of  $\text{Cl}^-$  has not reached the region beyond the “front”. If it is assumed that in the region up to  $z = z_{\text{Cl}}^-$  the adsorption–reaction of  $\text{Cl}^-$  in the solid phase far prevails over its desorption, i.e. that the value of  $\alpha$  in eq. (12) is much larger than unity (in reality,  $\alpha$  assumes values between 3 and 10), the term  $\sigma/\alpha$  in eq. (12) may be neglected. Then, the requirement that the net adsorption–desorption rate,  $\xi$ , is

zero for  $z$  between 0 and  $z_{\text{Cl}}^-$ , implies that throughout the diffusion–adsorption region  $\sigma$  is equal to 1.0. This means that all the adsorption–reaction of  $\text{Cl}^-$  takes place instantaneously at the location of the front, which is consistent with the very high value of  $\Phi$ .

Setting in the RHS of eq. (23)  $\sigma = 0$  at  $z = z_{\text{Cl}}^+$  and  $\sigma = 1$  at  $z = z_{\text{Cl}}^-$ , we obtain

$$z_{\text{Cl}} dz_{\text{Cl}} = \frac{1}{\beta} d\tau. \quad (24)$$

Equation (24) can be integrated over the period of time,  $\tau$ , required for the distance of the “front” from the surface to reach the value  $z_{\text{Cl}}$ :

$$\int_0^{z_{\text{Cl}}} z_{\text{Cl}} dz_{\text{Cl}} = \frac{1}{\beta} \int_0^\tau d\tau$$

i.e.

$$z_{\text{Cl}} = \sqrt{2\tau/\beta}. \quad (25)$$

Equation (25), along with the assumed linear variation of  $\lambda$ , from 1 at the surface to 0 at  $z = z_{\text{Cl}}$ , can give also the time of exposure of the concrete surface to  $\text{Cl}^-$  required for reaching the threshold concentration of  $\text{Cl}^-$  and depassivation of the steel bars.

#### 4. DETERMINATION OF MODEL PARAMETERS AND MODEL VERIFICATION

Papadakis *et al.* (1991a, 1992a) have presented theoretical and/or semiempirical computational procedures and expressions for the determination of concrete parameters of interest here, such as degree of pore saturation,  $f$ , concrete porosity,  $\epsilon$ , etc., in terms of the compositions of cement and concrete. Additional parameters required by the present model are the effective diffusivity of  $\text{Cl}^-$  in partially saturated concrete, the kinetic constant  $k_a$ , the equilibrium constant  $K_{\text{eq}} = k_a/k_d$  and the saturation concentration of  $\text{Cl}^-$ ,  $[\text{Cl}^-(\text{s})]_{\text{sat}}$ . These parameters depend on the composition of cement and concrete and on the type of positive ions of the chlorides. Among these parameters  $k_a$  seems to be the less important, as it does not enter the simplified model, eqs (19) and (20).

Parameters  $[\text{Cl}^-(\text{s})]_{\text{sat}}$  and  $K_{\text{eq}}$  can be determined from the slope and the intercept of straight lines fitted to experimental data on steady-state final concentrations of  $\text{Cl}^-(\text{aq})$  and  $\text{Cl}^-(\text{s})$  according to eq. (7), in concrete samples with known initial concentrations  $[\text{Cl}^-(\text{aq})]_{\text{in}}$  and  $[\text{Cl}^-(\text{s})]_{\text{in}}$ . Measurements of this type have been performed by Pereira and Hegedus (1984) and by Diamond (1986). The first authors measured through a colorimetric method the final liquid-phase concentration of  $\text{Cl}^-$  in crushed concrete placed in a solution of known initial concentration of NaCl. Diamond (1986), on the other hand, prepared cement paste samples with mixing water of known initial concentrations in NaCl or  $\text{CaCl}_2$  and measured the concentration of  $\text{Cl}^-$  in the liquid phase at various times after mixing, by extracting the pore water, which according to Tritthart (1989) is the most reliable method of measuring  $[\text{Cl}^-(\text{aq})]$ , and then  $[\text{Cl}^-(\text{s})]$ .

Values of  $K_{eq}$  and  $[Cl^- (s)]_{sat}$  determined in this way by Pereira and Hegedus (1984) for their own samples and in the present work [Fig. 1(a)] for the samples and tests of Diamond (1986) are listed in Table 1, along with information on concrete composition and porosity. The parameter values for the tests by Diamond show strong dependence of the cation of the chloride salt. Table 1 presents also the values of  $D_{e,Cl^-}$  and  $k_a$  selected by Pereira and Hegedus for their two concrete materials on the basis of fitting the complete set of equations, eqs (4)–(6), to their one-dimensional diffusion–adsorption test results on initially  $Cl^-$ -free concrete specimens immersed in water of constant chloride concentration. Finally Table 1 gives the optimal value of  $k_a$  selected herein to fit the test results of Diamond in the transient phase of an experiment with  $CaCl_2$  in the mixing water. The fitting was pursued in a trial-and-error fashion by numerical integration of eqs (4)–(6) without the differential term with respect to the space variable, taking also into account the strong dependence of the porosity  $\epsilon$  on age after casting, according to Papadakis *et al.* (1991a). The achieved fitting for the experimental

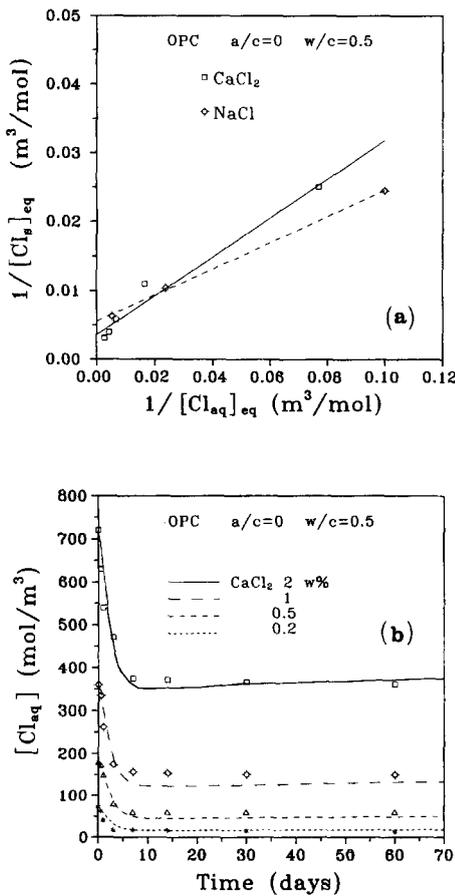


Fig. 1. Fitting of experimental data (Diamond, 1986) by the model and parameter estimation: (a) steady-state results and fitting of eq. (7); (b) transient results and fitting of eqs (4)–(6).

Table 1. Values of physicochemical parameters for different concrete mixes (reported by Pereira and Hegedus, denoted by (1), or fitted herein to the data by Diamond, (2))

Tests by	Concrete compos. <sup>†</sup>		$\epsilon$	Salt solution (% wt)	$D_{e,Cl^-}$ ( $m^2/s$ )	$[Cl^- (s)]_{sat}$ (mol/ $m^3$ concr)	$K_{eq}$ ( $m^3$ concr/mol)	$k_a$ ( $m^3$ concr/mol/s)
	w/c	a/c						
(1)	0.65	5.85	0.106	NaCl 26	$8 \times 10^{-12}$	214	$1.64 \times 10^{-2}$	$1 \times 10^{-5}$
(1)	0.54	4.57	0.102	NaCl 13	$3.5 \times 10^{-12}$	240	$1.20 \times 10^{-2}$	$1.5 \times 10^{-5}$
(2)	0.50	0	0.52–0.32	NaCl 26	—	180	$9.4 \times 10^{-2}$	—
(2)	0.50	0	0.52–0.32	CaCl <sub>2</sub> 13	—	601	$1.3 \times 10^{-2}$	$1 \times 10^{-8}$

<sup>†</sup>w, c, a: weight of water, cement and aggregates per unit volume of concrete.

results on the evolution of  $[\text{Cl}^- (\text{aq})]$  with time after mixing is shown in Fig. 1(b). The difference between model predictions and test results lies mainly in the steady state, which is controlled by the fitted values of  $K_{\text{eq}}$  and  $[\text{Cl}^- (\text{s})]_{\text{sat}}$  [see Fig. 1(a)]. The transient is reproduced well, but less well than in Pereira and Hegedus for their own tests. This last difference may be due to the fact that the transient phase lasts about 5 to 6 days, during which the concrete is in very early age and still setting. Accordingly the process of cement hydration may be controlling, rather than the relatively fast process of chloride adsorption and reaction, both in terms of the strong and relatively uncertain evolution of porosity  $\varepsilon$  with age and in terms of the possibly large difference in the  $\text{Cl}^-$  adsorption and reaction rates in fully vs partially hydrated cement. On the other hand, the absence of  $k_a$  from the simplified model, eqs (19) and (20), indicates that this is not a very important parameter for the adsorption-diffusion boundary value problem. This is demonstrated in Fig. 2, which compares the experimental data by Pereira and Hegedus and the predictions of the simplified model, which is equivalent to  $k_a = 0$ . Agreement with the test results is at least as good as achieved by Pereira and Hegedus using the complete model with the values of  $k_a$  listed in Table 1.

The approximate solution according to eqs (21) and (25), which assumes formation of a "front", is also shown in Fig. 2, by the straight line connecting the point of the externally imposed concentration at  $x = 0$  to the point of zero concentration at the value of  $z_{\text{Cl}}L$  determined from eq. (25). In general the approximate linear solution underestimates the  $\text{Cl}^-$  concentration throughout, because diffusion of  $\text{Cl}^- (\text{aq})$  is slowed down by the larger amount of chlorides considered to be adsorbed to full saturation of the solid phase, without any desorption back to the aqueous one. The case in Fig. 2 corresponding to 26%  $\text{Cl}^-$  by weight is an exception, because there the exact

concentration of  $\text{Cl}^-$  is strongly affected by the boundary condition at the plane of symmetry of the concrete slab at  $x = 2.5$  cm, while the approximate solution neglects the presence of such a plane of symmetry.

In noncarbonated concrete in normal marine or de-icing salt environments, the threshold value of  $[\text{Cl}^- (\text{aq})]$  which causes depassivation of the steel bars is not very much smaller than the externally imposed concentration of  $\text{Cl}^- (\text{aq})$  at the concrete surface,  $[\text{Cl}^- (\text{aq})]_0$ . Such values of the chloride concentration lie in the quasi-linear part of the exact variation of  $\text{Cl}^- (\text{aq})$  with distance from the surface. Therefore, in such cases the linear approximation of Section 3.2.4 is a reasonably accurate means for the assessment of the risk of bar depassivation, despite its lack of accuracy over the part of concrete where the concentration of  $\text{Cl}^- (\text{aq})$  is low.

### 5. PARAMETRIC STUDIES

Sensitivity analyses and parametric studies were performed using the simplified model, eqs (19) and (20), for a concrete slab with ordinary Portland cement (OPC), water-cement ratio  $w/c = 0.65$  and aggregate-cement ratio  $a/c = 6$ . This is the composition of the first specimen of Pereira and Hegedus (1984) and hence for fully saturated concrete the  $D_{e,\text{Cl}^-}$  and  $K_{\text{eq}}$  equal  $8 \times 10^{-12} \text{ m}^2/\text{s}$  and  $1.74 \times 10^{-2} \text{ m}^3 \text{ concr/mol}$ , respectively.

Figure 3 shows the time evolution of the dimensionless concentrations of  $\text{Cl}^-$  in the solid phase,  $\sigma$ , and in the liquid phase,  $\lambda$ , as a function of  $z$ , for a saturated slab continuously exposed on both sides to seawater ( $[\text{Cl}^- (\text{aq})]_0 = 590 \text{ mol/m}^3$ ). As in any diffusion problem, the concentrations decrease exponentially with distance from the exposed surface only at the beginning of the exposure, tending then to uniform concentration across the thickness after a long time.

Figures 4–7 show the results of sensitivity analyses with respect to  $D_{e,\text{Cl}^-}$ ,  $K_{\text{eq}}$ ,  $[\text{Cl}^- (\text{s})]_{\text{sat}}$  and  $L$ . Results

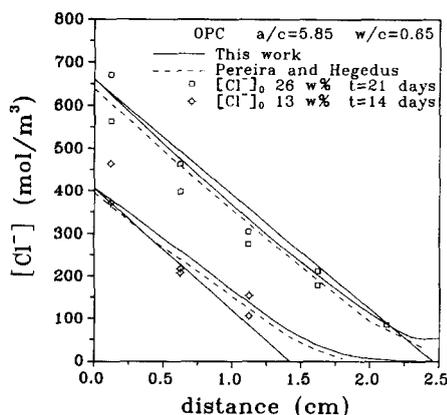


Fig. 2. Comparison of predictions of the simplified model of this work [solid curves: eqs (19) and (20), solid straight lines: eqs (21) and (25)] with test data by Pereira and Hegedus (1984) and with their complete model results (dashed lines). Concentrations are total:  $[\text{Cl}^- (\text{s})] + \varepsilon f[\text{Cl}^- (\text{aq})]$ .

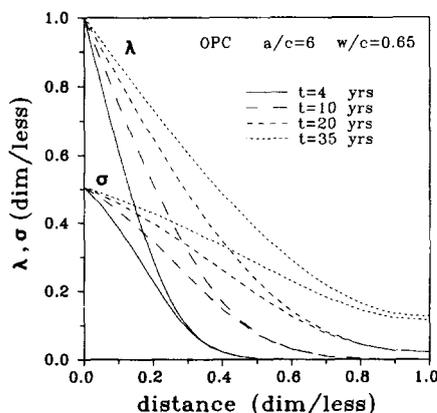


Fig. 3. Typical evolution of the dimensionless concentrations of  $\text{Cl}^-$  in the liquid ( $\lambda$ ) and solid ( $\sigma$ ) phases as a function of distance from the surface.

are presented in terms of the dimensionless  $\text{Cl}^-$  concentrations in the solid and the liquid phases at a distance  $x = 0.04 \text{ m}$  from the exposed surface (representative of reinforcement distance from the

outer surface of the concrete). The base case corresponds to the parameter values of the first specimen of Pereira and Hegedus (1984):  $D_{e,\text{Cl}^-} = 8 \times 10^{-12} \text{ m}^2/\text{s}$ ,  $K_{\text{eq}} = 1.74 \times 10^{-2} \text{ m}^3\text{concr}/\text{mol}$  and  $[\text{Cl}^- (\text{s})]_{\text{sat}} = 214 \text{ mol}/\text{m}^3\text{concr}$ , and to a total thickness  $2L$  of  $0.8 \text{ m}$ . Results suggest that the most important parameter is the diffusivity coefficient. In partially saturated concrete, which is the most interesting case from the point of view of steel corrosion after chloride penetration to the level of reinforcement, diffusivity values are expected to be between  $8 \times 10^{-12}$  and  $8 \times 10^{-13}$  and closer to the latter value. This means that results of interest will be close to the dotted lines in Fig. 4. The equilibrium constant,  $K_{\text{eq}}$ , is important only for the concentration of  $\text{Cl}^-$  in the solid phase (Fig. 5). However, as far as steel corrosion is concerned, the corrosion threshold depends on  $[\text{Cl}^- (\text{aq})]$ . Another important parameter is  $[\text{Cl}^- (\text{s})]_{\text{sat}}$ , which has a qualitatively similar but smaller effect as  $D_{e,\text{Cl}^-}$  (Fig. 6). The slab thickness,  $2L$ , is even less important, as shown in Fig. 7.

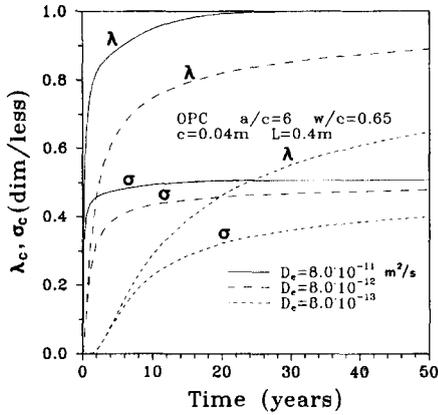


Fig. 4. Effect of  $\text{Cl}^-$  diffusivity,  $D_{e,\text{Cl}^-}$  and time on chloride concentration in the liquid ( $\lambda$ ) and solid ( $\sigma$ ) phases at the level of the reinforcement.

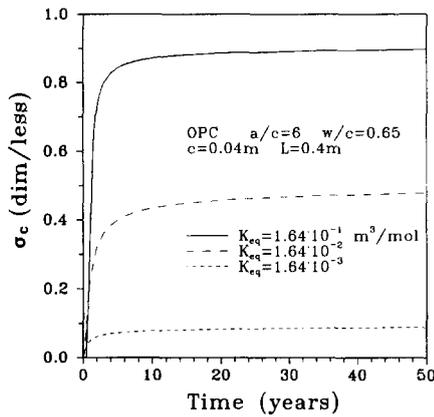


Fig. 5. Effect of equilibrium constant,  $K_{\text{eq}}$ , and time on the chloride concentration in the solid phase at the level of the reinforcement.

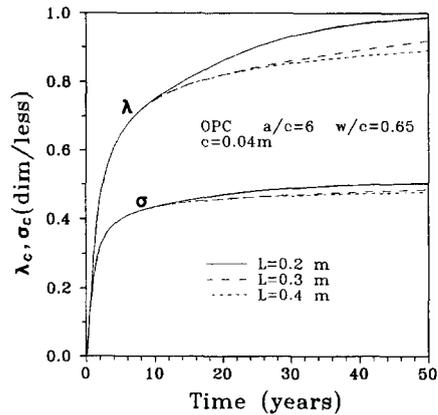


Fig. 7. Effect of slab thickness,  $2L$ , and time on chloride concentration in the liquid ( $\lambda$ ) and solid ( $\sigma$ ) phases at the level of the reinforcement.

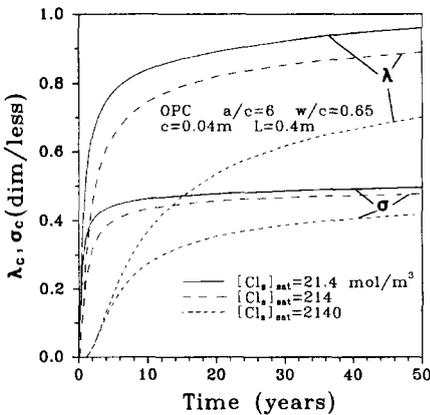


Fig. 6. Effect of saturation concentration of  $\text{Cl}^-$  in the solid phase,  $[\text{Cl}^- (\text{s})]_{\text{sat}}$ , and of time on the chloride concentration in the liquid ( $\lambda$ ) and solid ( $\sigma$ ) phases at the level of the reinforcement.

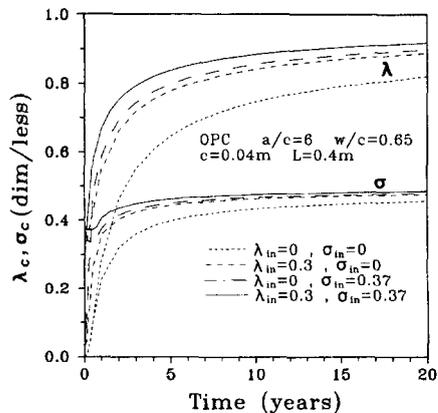


Fig. 8. Effect of the initial presence of  $\text{Cl}^-$  on the evolution of chlorides in the concrete.

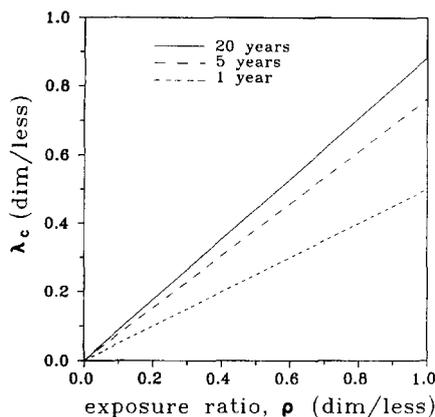


Fig. 9. Effect of interrupted exposure of the concrete surface to chlorides on their concentration at the level of the reinforcement.

dimensionless  $\text{Cl}^-$  concentrations at  $x = 0.04$  m for the base combination of parameter values above, when in addition to the constant exposure of the surface to an environment with  $[\text{Cl}^- (\text{aq})]_0 = 590 \text{ mol/m}^3$  of liquid phase (typical of seawater), there is either an initial concentration of  $\text{Cl}^-$  in the pore water of  $180 \text{ mol Cl}^-/\text{m}^3$  of water (equivalent to 1% of  $\text{CaCl}_2$  in the mixing water), or an initial concentration of  $80 \text{ mol Cl}^-/\text{m}^3$  of concr (corresponding to a volume content of  $\text{NaCl}$  in the concrete of 0.5%), or both. In all cases the asymptotic values of concentrations are  $\lambda = 1$  and  $\sigma = \alpha/(1 + \alpha)$ . The initial chloride concentration is important only in the very early stage of the diffusion-reaction process. Since the time evolution of the initial-conditions-dependent part of the problem is independent of the distance from the surface, the effect of  $\text{Cl}^-$  ingress will be predominantly closer to the surface and less important near the center.

The final parametric study refers to cycles of exposure of the slab surface to chlorides (Fig. 9). The total period of time was divided into a large number of intervals of length  $T$ , during the initial part  $\rho T$  of which the surface is considered to be exposed to chloride ingress, while during the rest,  $(1 - \rho) T$ , it is not. Pore saturation conditions, though, were not considered to be affected by the change in exposure conditions. The problem was solved numerically, as a mixed (boundary condition-initial condition) one. Figure 9 shows that the dimensionless concentration of  $\text{Cl}^-$  in the liquid phase at a distance of 0.04 m from the surface increases linearly with the "exposure ratio"  $\rho$ , independently of the total duration  $T$  of the exposure-nonexposure cycle. This means that what matters over periods of time much longer than the exposure cycle, is the total amount of  $\text{Cl}^-$  which enters through the exposed surface.

## 6. CONCLUSIONS

The physicochemical processes of diffusion of dissolved chlorides in partially filled pores of concrete

and of their adsorption-binding-desorption by the constituents of the hardened cement paste can be modeled by a single nonlinear diffusion-type partial differential equation for the concentrations of chloride ions in the aqueous phase of the pores plus a linear algebraic expression for the concentration of  $\text{Cl}^-$  in the solid phase of concrete in terms of that in the aqueous. The parameters of the differential equation are not only the diffusivity of  $\text{Cl}^-$  in partially saturated porous concrete but also the saturation concentration of  $\text{Cl}^-$  in the solid phase, the equilibrium constant for chloride adsorption (equal to the ratio of the kinetic constants for adsorption and desorption of  $\text{Cl}^-$  between the solid and the aqueous phase) and the porosity and the degree of pore saturation of concrete. Fitting of the model to experimental data allows estimation of the physicochemical parameters, some of which turn out to depend not only on the composition and structure of the concrete but also on the type of positive ion in the chloride ( $\text{Na}^+$  vs  $\text{Ca}^{2+}$ ).

The results of parametric studies performed on the basis of the nonlinear differential equation developed herein suggest that the effective diffusivity of  $\text{Cl}^-$  in the concrete is the most important parameter, followed by the saturation concentration of adsorbed-bound  $\text{Cl}^-$  in the solid phase. The equilibrium constant for  $\text{Cl}^-$  adsorption-desorption and the thickness of concrete beyond the cover of the reinforcement are relatively unimportant. In the presence of a persistent external source of chlorides, such as de-icing salts and seawater or salt-laden air or mist reaching the concrete surface, the initial concentration of chlorides in the bulk concrete, due, e.g. to the use of chloride-containing admixtures or seawater or beach aggregates in the concrete mix, is relatively unimportant. Finally, if the exposure of the concrete surface to chlorides is not continuous but periodic, whereas the amount and the distribution of water in the pores does not change, the evolution of the chloride content in the aqueous and the solid phase of concrete depends on the total quantity of chlorides entering the concrete from the environment through its surface and not on its exact variation with time.

The assumption of the formation of a "chlorination front" is well justified on reaction engineering grounds and provides a simple, yet accurate, analytical approximation to the rigorous numerical solution.

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## NOTATION

$a/c$	aggregate-to-cement ratio, by weight
$c$	distance of reinforcement from the outer surface of concrete, m
$\text{C}_3\text{A}$	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$
$\text{C}_4\text{AF}$	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$

$[Cl^- (aq)]$	molar concentration of $Cl^-$ in the aqueous phase of concrete, $mol/m_1^3$	concr	quantities referring to the total concrete volume
$[Cl^- (s)]$	molar concentration of $Cl^-$ in the solid phase of concrete, $mol/m_{concr}^3$	in	quantities referring to $t = 0$
$[Cl^- (s)]_{sat}$	saturation molar concentration of $Cl^-$ in the solid phase, $mol/m_{concr}^3$	$l$	quantities referring to the aqueous-phase volume
CSH	calcium-silicate-hydrate		
$D_{e,Cl^-}$	effective diffusivity of $Cl^-$ in concrete, $m^2/s$		
$f$	fraction of pore volume filled with water		
$k_a, k_d$	kinetics constants of $Cl^-$ adsorption and desorption, respectively, $m_{concr}^3/s \text{ mol}$ , $1/s$		
$K_{eq}$	equilibrium constant for chloride adsorption, $m_{concr}^3/mol$		
$L$	distance between outer surface and axis of symmetry, $m$		
$r$	total rate of $Cl^-$ binding in concrete, $mol/m_{concr}^3 s$		
$r_a, r_d$	rate of $Cl^-$ adsorption and desorption, respectively, $mol/m_{concr}^3 s$		
$t$	time, $s$		
$T$	period of the complete exposure–nonexposure cycle, $s$		
$w/c$	water-to-cement ratio, by weight		
$x$	distance from the outer surface of concrete, $m$		
$z$	dimensionless distance		
<b>Greek letters</b>			
$\alpha$	$= efK_{eq}[Cl^- (aq)]_0$		
$\beta$	$= [Cl^- (s)]_{sat}/ef[Cl^- (aq)]_0$		
$\varepsilon$	concrete porosity		
$\lambda$	dimensionless concentration of $Cl^- (aq)$		
$\xi$	dimensionless total rate of $Cl^-$ binding in concrete		
$\rho$	ratio of the exposure time to the total time of a complete cycle		
$\sigma$	dimensionless concentration of $Cl^- (s)$		
$\tau$	dimensionless time		
$\Phi$	Thiele modulus $(= r_{max}L^2/[Cl^- (aq)]_0 D_{e,Cl^-})^{1/2}$		
<b>Subscripts</b>			
0	quantities referring to $x = 0$		
$\infty$	quantities referring to $t \rightarrow \infty$		
$c$	quantities referring to the level of the reinforcement		
$cl$	quantities referring to the level of the "chlorination front"		

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