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NUMERICAL MODELING OF ELECTROCHEMICAL CHLORIDE REMOVAL FROM CONCRETE

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ABSTRACT

A numerical model of electrochemical chloride removal from concrete (desalination) based on the Nernst-Planck and the Laplace equations is proposed. The model relies on experimentally derived chloride transport number profiles. It is shown that the model can make realistic predictions of both the chloride removed and the chloride remaining in concrete made with admixed sodium chloride. *© 1998 Elsevier Science Ltd*

Introduction

The cost, worldwide, of the repair and maintenance of concrete structures suffering from chloride-induced corrosion of steel reinforcement is in excess of £ 4,000 million per annum (1). A technique for arresting this corrosion by removing the offending chloride electrochemically is now being applied to some concrete structures.

This technique uses an electrode (anode) that is fixed to the surface of the concrete and contained within a liquid electrolyte (anolyte). A direct current is then passed between the anode and the embedded steel reinforcement, which acts as a cathode. The current results in chloride ions being drawn towards the anode where they eventually pass out of the concrete into the anolyte.

The feasibility of using this technique on real structures was first investigated in 1976 (2). However, it was only in 1987 that it was commercially introduced, and consequently there are still no long-term field data available on the effectiveness of the treatment (3). Numerical modeling could be used to give an immediate assessment of effectiveness.

This paper reports on a preliminary study undertaken to numerically model electrochemical chloride removal (also termed desalination) from concrete. Previous works on this aspect are limited. For example, Banfill (4) has proposed a crude model for calculating chloride removal rates during desalination. The work by Andrade et al. (5) is more detailed and enables the duration of the treatment in concrete containing internal and external chloride to be estimated. Both works are based on the Nernst-Planck equation discussed below.

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Processes in Chloride Extraction

The general equation that describes transport processes in solution is the Nernst-Planck equation. It assumes that the total flux J (mol/m^2·s), is made up of three components, namely, diffusion, migration, and convection, expressed as:

$$-J(x) = D_j \frac{dC_j(x)}{d(x)} + \frac{ZF}{RT} D_j C_j \frac{dE(x)}{dx} + C_j V(x) \tag{1}$$

The first term on the right of Eq. 1 is the contribution due to diffusion and the third is the contribution due to convection. The contribution of diffusion in concrete is small at the potentials normally used in desalination and can safely be neglected. Likewise the contribution due to convection can be ignored, because it is unlikely that there are appreciable temperature gradients to cause convection (4,5). Only the second term is of principal importance in the electrochemical desalination process, and Eq. 1 therefore reduces to:

$$-J(x) = \frac{ZF}{RT} D_j C_j \frac{dE}{dx} \tag{2}$$

where Z is the oxidation number of the migrating species, F is the Faraday's constant (96500 coulombs/equivalent), R is the universal gas constant (8.3 Joule/mol K), T is absolute temperature (K), E/x is the strength of the electric field between the anode and cathode (V/m), C_j is the bulk concentration of ion j (mol/m^3), and D_j is the diffusion coefficient of ion j (m^2/s).

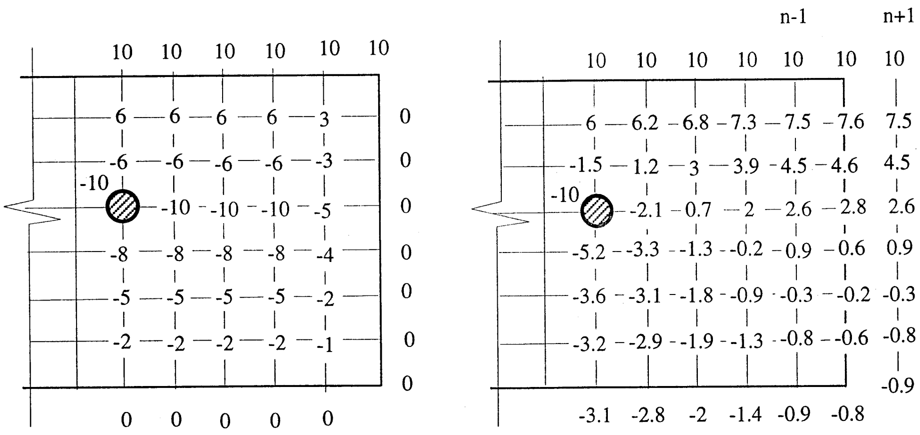
Numerical Model

Equation 2 gives no information on the actual flow path of ions in concrete. This problem can be overcome, however, if the potential and current distributions in the specimen are known. A method of predicting the likely form of these distributions entails using a finite difference solution to the Laplace equation (6).

The actual procedure involves dividing the specimen cross-section into a mesh and assigning voltages to each of the nodes. For example, if a 20 V pd exists between the anode surface and the cathode bar, the initial estimates of the potentials at the nodes are as indicated in Figure 1a. The absolute values of the potentials are irrelevant; only the potential gradient is important. Hence, the potential at the cathode is assumed to be -10 V, whereas the potential at the anode is assumed to be $+10$ V. The initial potentials at the sides and bottom of the specimen are 0 V. The intermediate potentials are obtained by linear interpolation. Finite difference calculations are then performed using potential values of neighbouring points by a procedure described by Smith (6) to give the steady-state potentials shown in Figure 1b.

To achieve normal incidence of the equipotential lines at the specimen boundaries, fictitious nodes are added. At the end of each cycle of iterations, the potential of the fictitious node ($n + 1$) is equated to the potential of the node immediately inside the specimen ($n - 1$) (Fig. 1b). Figure 2 shows the resulting equipotential contours.

The current flow lines are then drawn at constant intervals such that they intersect the equipotential and specimen boundaries at right angles to form a flow net of curvilinear "square" shapes. The current lines are constructed by a procedure described by Holtz and



(a) Assumed potentials (b) Steady state potentials

FIG. 1.
Initial and steady state potentials, assuming that a 20 V pd exists between the anode surface and the cathode bar.

Kovacs (7). By using this technique, the flow net shown in Figure 3 was obtained. To calculate the actual flow in specific channels, it is necessary to divide the flow channels into segments such that the time required for ions to flow between successive segments is equal, giving the final flow net shown in Figure 4.

Equation 2 can then be used to calculate the ionic flow during desalination. It should be remembered that this equation describes the flow of all charged ions in solution and not just chloride ions. To predict the flow of chloride ions during desalination, Eq. 2 needs to be multiplied by the chloride ion transport number (see below). To simplify the analysis, it was assumed that the chloride ion diffusion coefficient remains constant during desalination. It was also assumed that the electric field does not vary during desalination. This was considered to be reasonable, based on earlier results which showed that the current does not change

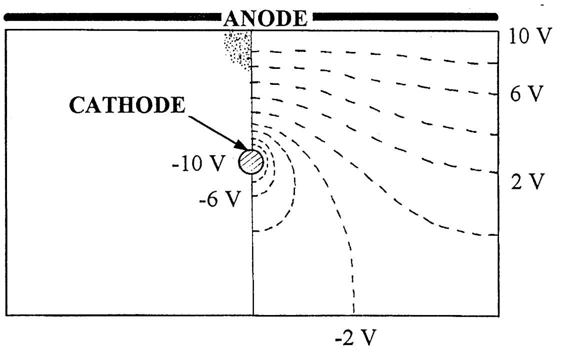


FIG. 2.
Equipotential lines, assuming that a 20 V pd exists between the anode surface and the cathode bar.

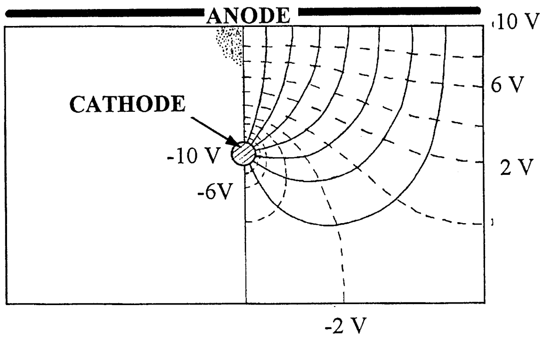


FIG. 3.
Equipotential and current flow lines.

significantly with time of treatment when an electric field of 20 V is applied between the anode and cathode (8).

The model assumes that electrochemical desalination is a steady-state process, although clearly this is not the case in practice because the chloride content reduces with time of treatment (9) However, provided that the ionic flow between successive segments of the flow net (Fig. 4) is calculated for short intervals of time (say, 50 hrs), the change in chloride concentration is small and hence approximation of steady-state conditions is reasonable.

Transport Number

The transport number of an ion is defined as the fraction of total current which is carried by that ion in an electrochemical process.

The chloride ion transport number can be derived theoretically if the conductivities and concentrations of the various ions present in concrete pore solution are known. On this basis, Banfill (4) has suggested that the chloride ion transport number is about 0.2, whereas Andrade (9) suggests a value of 0.338. However, it is unlikely that the transport number is fixed with time, because the composition of the pore solution will vary with time. This may explain the results of previous investigations, which have shown that the rate of chloride removal decreases with increasing time of desalination (8).

An alternative approach, which was used by Bennett et al. (10) to estimate the chloride ion

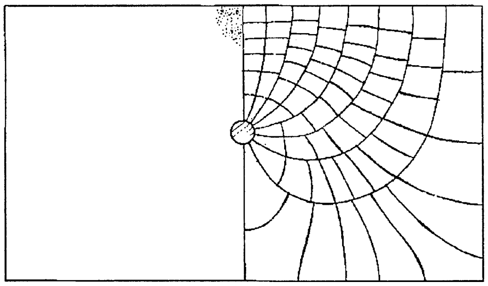


FIG. 4.
Flow net used to predict ionic flow.

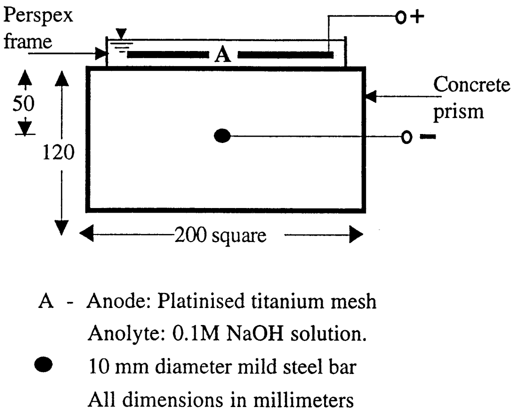


FIG. 5.
Test specimen and desalination set-up.

transport number, relates the amount of chloride removed to the anolyte with the corresponding amount of charge passed. The chloride ion transport number (t_{Cl}) is then given by:

$$t_{Cl} = NF/It \tag{3}$$

where F is Faraday's constant and N is the number of moles of chloride in the anolyte resulting from the passage of current I (amps) for t seconds.

The following describes the experimental work that was undertaken to elucidate the relationship between transport number and operating time, and to verify the theoretical approach outlined above for predicting both the chloride in the anolyte and the chloride remaining in concrete during desalination.

Experimental Procedure

Three concrete prisms (A, B, and C), 200 mm × 200 mm × 120 mm high, each containing one 10-mm diameter mild steel bar at a cover depth of 50 mm, were subject to electrochemical chloride removal. A perspex frame cast into the top face of each prism served to contain the anode/anolyte system (Fig. 5).

The composition of the concrete is shown in Table 1. Prisms A, B, and C were cast using concrete dosed throughout with, respectively, 2%, 3%, and 4% Cl (by weight of cement) from sodium chloride. All the prisms were desalinated from the top face by passing a direct current between the embedded reinforcing steel and the anode system consisting of an inert

TABLE 1
Mix details (proportions by weight).

OPC	1.00
Sand (zone 3)	2.40
10 mm aggregate (limestone)	2.90
water	0.65

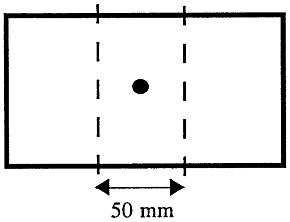


FIG. 6.
Sample for dry grinding.

platinised titanium mesh immersed in 0.1 M NaOH solution (Fig. 5). A fixed potential of 20 V was used throughout.

The NaOH solution was replaced every 2 to 3 days to maintain alkalinity and prevent chlorine gas from being evolved from the electrolyte. Desalination was normally continued until the rate of chloride extraction was negligible.

The chloride removed during the treatment was determined periodically by potentiometrically titrating 2 mL aliquots of the electrolyte with a silver nitrate solution using a chloride ion selective electrode, in accordance with the method described by Berman (11). Two replicates of each prism were tested.

At the end of the treatment, a 50-mm wide slice was removed from the centre of each prism using a diamond saw (Fig. 6). Each slice was ground in 2-mm depth increments and the dust from each depth increment collected separately. The dust samples were then oven dried at 105°C. Finally, the samples were treated with nitric acid and their chloride contents determined by potentiometric titration.

Results and Discussion

Chloride Transport Number Profiles

Figure 7 shows the relationships between chloride transport number and treatment time obtained by desalinating prisms A, B, and C. It can be seen that the chloride transport number is not fixed but reduces with decreasing chloride content. Also, the chloride transport number reduces with increasing treatment time. The latter finding is in agreement with the results presented by Bennett et al. (10).

Chloride in the Anolyte

The chloride extracted during desalination was predicted by applying Eq. 2 multiplied by the appropriate transport number from Figure 7 to successive segments of the flow net in Figure 4.

This enabled both the total chloride removed into the anolyte (Fig. 8) together with the chloride remaining in the concrete prisms to be calculated for given intervals (approximately 50 h) of desalination (see below). Figure 8 also shows the actual amount of chloride removed from prisms A, B, and C during desalination. It can be seen that, generally, there is good agreement between the actual and predicted chloride levels in the anolyte.

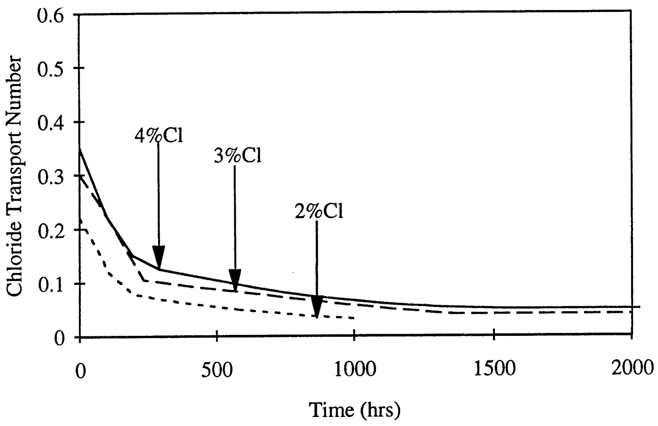


FIG. 7.
Chloride transport number profiles.

In Eq. 2, the chloride ion diffusion coefficient was assumed to be 4×10^{-12} m^2/s. Values for C were estimated from Figure 9 (12). In line with previous findings (8), it was further assumed that only free chloride is removed during desalination. The proportion of free and bound chloride was estimated from the following (13):

$$F = 0.88T - 0.23 \tag{4}$$

where F and T are, respectively, the free and total chloride content (% by weight of cement).

The chloride concentration at the surface of the concrete prism was assumed to be zero throughout the treatment. This condition was achieved in practice by renewing the anolyte every 2 or 3 days as noted in the experimental procedure.

Chloride in the Concrete

Figures 10 through 12 show the initial (chain-link line), actual (dashed line), and predicted (solid line) chloride levels with depth of specimen in the 50-mm slices removed from prisms

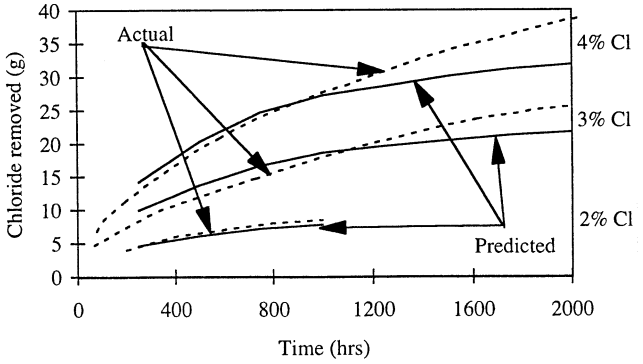


FIG. 8.
Chloride removed from prisms containing 2%, 3%, and 4% Cl from NaCl.

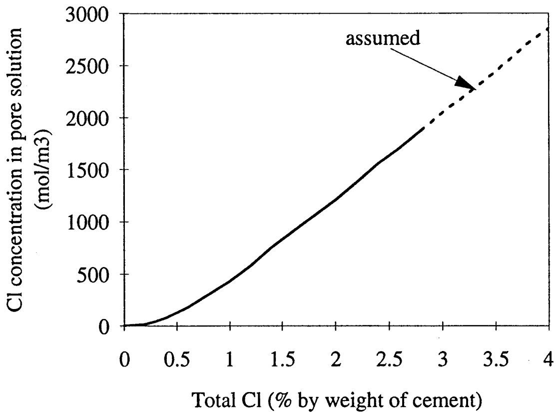


FIG. 9.
Pore solution chloride concentration vs. total chloride content for 28-day-old OPC pastes with w/c = 0.5 containing internal chloride from NaCl(12).

A, B, and C after desalination. Generally, it can be seen that the proposed model can make fairly realistic predictions of the amount of chloride remaining in concrete.

The profiles showing the actual chloride levels in concrete suggest that virtually all the free chloride above the bar is removed during desalination and also that much chloride is removed below the bar. These features are mirrored in the chloride profiles obtained via the numerical model.

More significantly, the profiles showing the actual level of chloride remaining in concrete indicate that even prolonged treatment does not result in removal of all the chloride around the reinforcing steel. This aspect is particularly noticeable in the prisms dosed with 3% and 4% chloride where the concentration around the reinforcing bar appears to be above the normally accepted threshold value needed for corrosion initiation. Nevertheless, half-cell potential readings after desalination of the prism with 4% Cl indicated that corrosion had

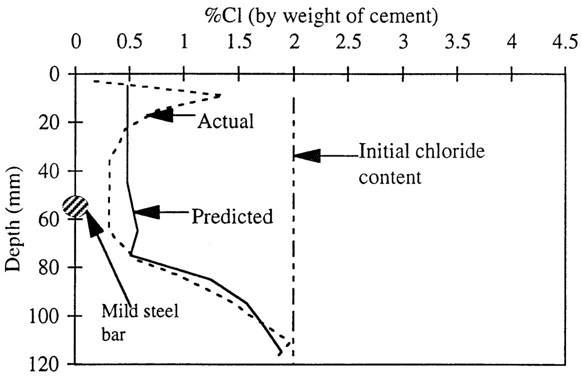


FIG. 10.
Actual and predicted chloride remaining in prisms containing 2% Cl from NaCl after 1000 h of desalination.

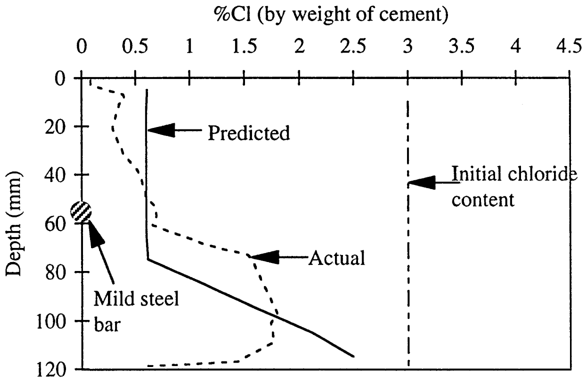


FIG. 11.
Actual and predicted chloride remaining in prisms containing 3% Cl from NaCl after 2000 h of desalination.

stopped (Fig. 13). This suggests that passivation had been restored, probably due to the raised concentration of hydroxyl ions at the cathode.

Conclusions

1. Electrochemical chloride removal from concrete can be modeled assuming steady state conditions, using the Nernst-Planck and Laplace equations in order to make realistic predictions of both the chloride passing out of the concrete into the anolyte and the chloride remaining in the concrete with treatment time.
2. The chloride transport number is not fixed but decreases with increasing time of desalination and decreasing chloride content.
3. Prolonged desalination will result in the removal of most of the free chloride above the reinforcing steel and a large proportion of chloride below the bar. More significant is the

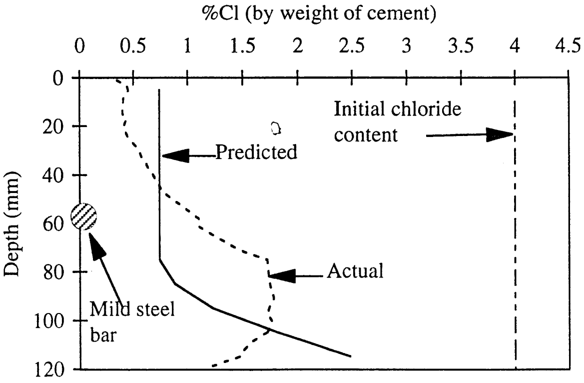


FIG. 12.
Actual and predicted chloride remaining in prisms containing 4% Cl from NaCl after 2000 h of desalination.

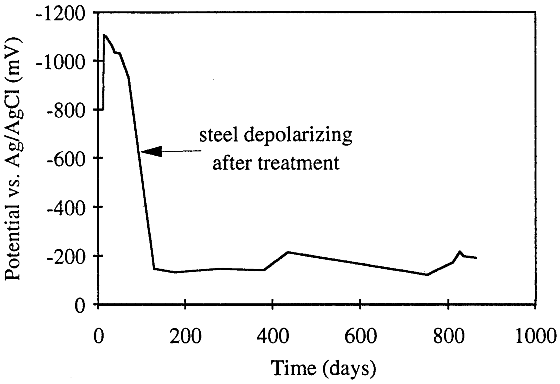


FIG. 13.
Potential readings for prism C containing 4% Cl after desalination.

fact that the chloride content around the reinforcement may still exceed the threshold value needed for corrosion initiation, particularly in cases where the chloride content is high.

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