Pergamon

Cement and Concrete Research, Vol. 25, No. 4, pp. 727-740, 1995

0008-8846/95 $9.50+.00

0008-8846(95)00063-1

MATHEMATICAL MODELLING OF ELECTROCHEMICAL CHLORIDE EXTRACTION FROM CONCRETE

C. Andrade*, J.M. Diez**, A. Alamán* and C. Alonso*

* Institute of Construction Science
"Eduardo Torroja". CSIC. Madrid. Spain.

** Mining Engineering Faculty Politechnical
University. Madrid. Spain.

(Refereed)
(Received April 6, 1944; in final form February 28, 1995)

REFEREED PAPERS

ABSTRACT

Equations to calculate the duration of electrochemical chloride extraction have been proposed and solved for the case of a constant chloride concentration in the concrete or for a concentration following the error function trend.

In the case of constant initial chloride content, both potentiostatic and galvanostatic operation have being considered, while only the potentiostatic one was considered in the case of non-constant initial chloride profile. Potentiostatic operation has seemed to lead to an easier mathematical calculation. Numerical examples are given to illustrate the mathematical modelling and are also applied to experimental results previously published by Tritthart and Elsener.

INTRODUCTION

It was in 1973-1975 when Batelle Institute reported (1) the first trials on extracting chlorides from concrete bridge decks applying an electrical field between the reinforcement and an external anode placed on the surface of the concrete. Since then, several attempts were made (2)(3), although it is not until recently that the method has been commercialized and therefore, its application is spreading.

In spite of the increasing experience on its application to real structures, its efficency in cleaning the concrete is still discussed, and several theoretical aspects remain unknown. This is due mainly to the lack of a sound background on how an electrical field affects concrete pore solution chemistry, that is, how ions inside concrete pores move under the driving force of an electrical potential.

In a set of recent papers, some of the authors have published (4-7) an interpretation of this background and, therefore, they think that it is now feasible to undertake a theoretical approach to phenomena such as electrochemical chloride extraction or concrete realkalization.

In the present paper the chloride extraction is considered. First, the processes developing under the application of an electrical potential are described for the particular case of a corroding structure. Then, based in Fick's laws, the theoretical solutions of chloride removal are presented for two cases: a) the simplest case of having an internal chloride concentration constant along the cover, and b) when the chloride has penetrated the cover following a non-stationary process and presenting the known "error function" concentration profile. Numerical examples are given.

PROCESSES DEVELOPING DURING THE APPLICATION OF AN ELECTRICAL FIELD.

These processes have been described for a general case in (4) and (6), and some are also those occurring during cathodic protection (9). They are represented in figure 1 for the particular case of a concrete cover contaminated with chlorides.

As soon as the electricity is connected forcing the rebar to act as the negative pole (cathode), the processes developing may be:

Cathode

water electrolysis $2H_2O + 2e^- \rightarrow 2OH^- + H_2$ [1]

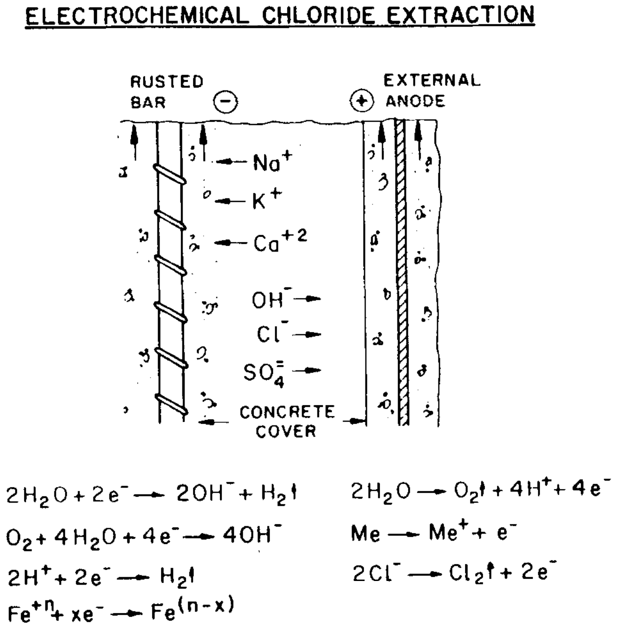

Figure 1. Reactions and processes developing during electrochemical chloride extraction.

oxygen reduction $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ **[2]**

proton reduction $2H^+ + 2e^- \rightarrow H_2$ **[3]**

ferrous/ferric
oxyde reduction $Fe^{+3} + e^- \rightarrow Fe^{+2}$ **[4]**

The two first processes are the most known whereas the two last are usually not mentioned. However, in the environment sourrounding a corroding steel rebar, the pH decreases (8) until a certain value in the acid zone is reached and, therefore, the hydrogen ions generated during the corrosion process:

$$Fe^{+2} + H_2O \rightarrow Fe(OH)_2 + H^+ \qquad [5]$$

may be reduced when an external current is applied.

The reduction of the oxides formed during the corrosion period has to be considered as well. Depending on the cathodic potential finally imposed, this reduction could stop at the level of converting all oxides onto ferrous ones, or even go into the total reduction, to metallic iron. This reduction will transform the normal brown-yellow colour of the rust into a dark green or black one, corresponding to ferrous hydroxydes or magnetite, or, as it was mentioned, to metallic state.

Anode

metal dissolution $Me \rightarrow Me^+ + e^-$ **[6]**

water electrolysis $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ **[7]**

chloride evolution $2Cl^- \rightarrow Cl_2 + 2e^-$

Whether the material used as anode is a corroding or a non corroding metal, all three processes or the last two ones, will respectively proceed.

As the metal ions induce the water hydrolysis:

$$Me^+ + H_2O \rightarrow MeOH + H^+ \qquad [8]$$

in the anodic surroundings an acidification will always be built up.

Electrolyte

All ions present in the pore solution that have been generated at the electrodes will move towards the counter pole.

This movement has to follow the mass transport law for electrolytes (Nernst-Plank) (4)(9), which states that the total net flow is the addition of:

Total flow = diffusion + migration + convection

$$-J(x) = D_j \frac{\partial C_j (x)}{\partial x} + \frac{ZF}{RT} D_j C_j \frac{\partial E (x)}{\partial x} + C_j V(x) \qquad [9]$$

where:

$J(x)$ = unidirectional flux of species j (mol/cm^2s)
D_j = diffusion coefficient of species j (cm^2/s)
∂C = variation of concentration (mol/cm^3)
∂x = variation of distance (cm)
Z_j = electrical charge of species j
F = Faraday's number ($cal/volt \cdot eq^{-1}$)
R = gas constant (cal/mol K)
T = absolute temperature (K)
C_j = bulk concentration of the species j (mol/cm^3)
∂E = variation of potential (V)
V = artificial or forced velocity of ion (cm/s)

The term migration is which takes into account the movements due to the application of a voltage, ΔE, and the convection one, any movement due to the mechanical (stirring) or thermal gradients.

In the case of concrete, **convection** is not expected unless some kind of "breathing" of the cover due to moisture gradients is operating. For the sake of simplification, convection is going to be neglected, although it might be considered in cases as the one shown in figure 2, where the maximum of chloride concentration is detected beyond the surface. This may be interpreted as a kind of leaching or moisture movements from the outside towards the interior of the concrete. As it has been aforementioned, this phenomenon is not taken into consideration in present paper.

Diffusion is also neglected in equation [9] because, as it was explained in (6), it has a negligible influence compared to migration. That is, as being the accelerating factor of migration the term $ZF\Delta E/RT$, its value for 1 volt is 40 and therefore, the diffusion of chlorides penetrating the concrete becomes, indeed, negligible.

Therefore, the unique term to be taken into consideration in Nernst-Plank equation is that one corresponding to migration. Thus the total flow (in steady state conditions) will be:

$$J = Dc \frac{ZF}{RT} \frac{dE}{dx} \qquad [10]$$

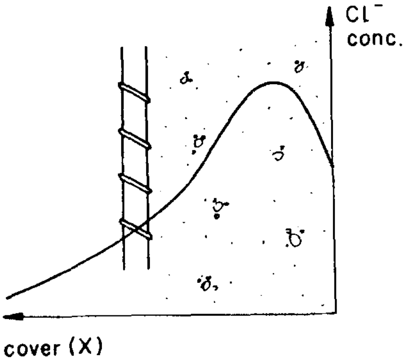

Figure 2. Frequent chloride profile in structures submitted to moisture cycling.

This is also named Nernst-Einstein equation, as it was this last author who developped it, and demostrated that the Diffusion Coefficient is a function of the electrolyte conductivity. Einstein presented the equation in its more general form (4):

$$D = \frac{RT}{nF^2}\Lambda_o \qquad [11]$$

Λ_0= equivalent conductivity

A final important feature to mention is that comparing equation [10] with first Fick's law, they are identical, except that [10] is multiplied by ZFdE/RT (6), and therefore:

$$D_{(mig)} = D_{(dif)}\,\frac{ZFdE}{RT} \qquad [12]$$

an expression which enables the mathematical solution of electrochemical chloride extraction.

It remains only to consider **initial** and **boundary** conditions for the mathematical solution in none stationary conditions of the extraction process. This will be dealt with next for the cases where:

1) the internal chloride concentration c_i = constant
2) the internal chloride profile follows the expression:

$$C_x = C_s\,(1 - erf\,\frac{x}{2\sqrt{Dt}}) \qquad [13]$$

MATHEMATICAL SOLUTION FOR CONSTANT CHLORIDE CONCENTRATION INSIDE THE CONCRETE

This possibility exists when the chlorides were added in the concrete mix. The extraction of chlorides in this case may be not easy providing the removable ones are only those between the external concrete surface and the rebar. However, for the sake of the calculation this practical aspect is not going to be considered here, and only mathematical expressions encountering the extraction law will be commented on.

The case can be dealt with as: 1) an extraction in which an external sink exists (8) or 2) considering that Cl^- ions are oxidized at the anode to Cl_2, so that the concentration of Cl^- becomes effectively zero at the anode surface (9). In this last case the potential or current applied has to be high enough to force the oxidation of chlorides at the anode.

Following the second assumption of considering a constant flux towards the exterior operating from a certain moment t= 0, Bard and Faulkner (9) present the solution of second Fick's law depending upon whether the test is potentiostatic or galvanostatic.

Potentiostatic test -

They (9) presume a planar electrode, an unstirred solution and a potential extreme enough to make none significant the kinetics of the oxidation process. Therefore, the calculation of the diffusion-limited current I, and the concentration profile C_x along the time, involves the solution of the equation:

$$\frac{\partial C_x}{\partial t} = D\frac{\partial^2 C_i}{\partial x^2} \qquad [14]$$

with the initial condition:

$$C_x(x,0) = C_i \qquad (for\ x>0) \qquad [15]$$

and the boundary conditions(semiinfinite media):

$$C_x(x\to\infty, t) = C_i \qquad [16]$$

$$C_x(0,t) = 0 \qquad (for\ t>0) \qquad [17]$$

being Ci = the initial chloride concentration inside the concrete.

The analytical solution gives rise to the following expression known as the **Cottrell equation [9]** which shows that the effect of depleting an electroactive species at the electrode surface is characterized by an inverse $t^{1/2}$ function.

$$I.\,t_{Cl} = \frac{nFAD^{1/2}C_i}{\pi^{1/2}t^{1/2}} \qquad [18]$$

A= metal area (cm^2)
I= current density (A/cm^2)
t_{Cl}= transference number of chlorides

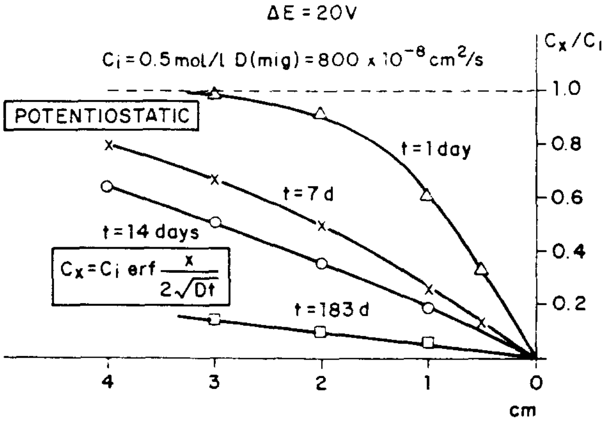

Figure 3. Chloride profiles during electrochemical removal under potentiostatic regime.

At the same time the concentration profile is given by:

$$C_x = C_i \; erf \left(\frac{x}{2\sqrt{Dt}} \right) \qquad [19]$$

which results to be the complementary expression of equation [13].

The pattern of ideal concentration profiles is shown in figure 3 for a D= 800x10^{-8} cm^2/sec, an applied voltage of 20 V and an initial Ci= 0.5 mol/l.

Galvanostatic test -

In the case of a controlled current experiment, the surface boundary condition is based on the known fluxes at the electrode surface while, in controlled potential methods, the concentration at x= 0 was what provided the boundary conditions.

Again considering a planar electrode, single electron transfer, unstirred solution, the initial condition and the first boundary condition for a current controlled test are the same equations [15] and [16] respectively. In addition, since the applied current I is known, the flux at the electrode surface is also known at any time, by the equation (new second boundary condition):

$$D \left(\frac{\partial C_i}{\partial x} \right)_{x=0} = \frac{I t_{cl}}{nFA} \qquad t>0 \qquad [20]$$

This boundary condition involving the concentration gradient allows the diffusion problem to be solved, in contrast with the concentration: potential boundary conditions required for controlled potential methods.

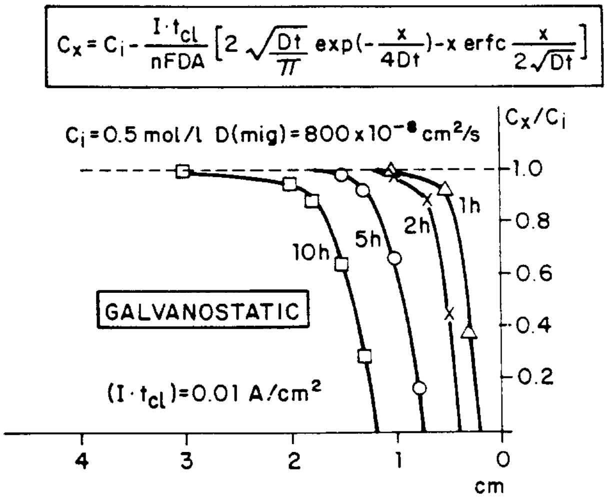

Figure 4. Chloride profiles during electrochemical removal under galvanostatic regime.

The concentration profile in this case results:

$$C_x = Ci - \frac{I\,t_{Cl}}{nFAD}\left[2\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}\exp\left(-\frac{x^2}{4Dt}\right) - x\,erfc\left(\frac{x}{2\sqrt{Dt}}\right)\right] \qquad \textbf{[21]}$$

The pattern of concentration gradients for D= $800\mathrm{x}10^{-8}$ cm^2/sec and (Ixt_{Cl})= 0.01 $\mathrm{A/cm}^2$, Ci= 0.5 mol/l, is given in figure 4.

Comparison of figure 4 with figure 3 shows that galvanostatic operation induces a different concentration profile depending upon the values selected: those in the figure are much steeper, but also they may be almost flat.

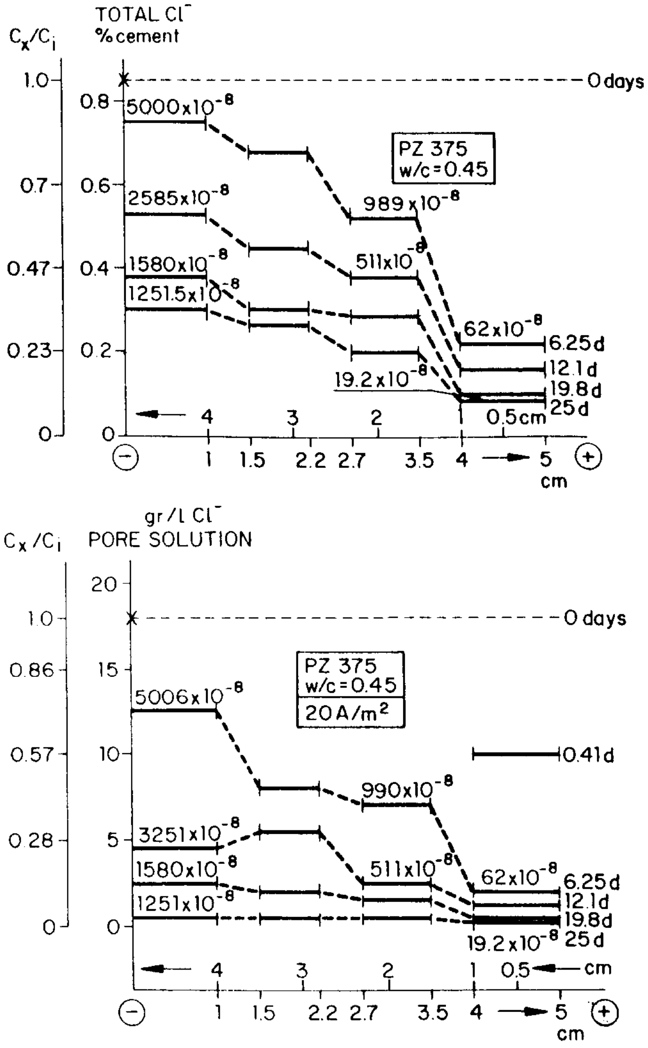

Figure 5. Tritthart (10) values of chloride profiles (total: upper and free: bottom part of the figure) under galvanostatic treatment. Numbers indicate D values obtained by means of equation [21]. Care has to be introduced on their interpretation.

Another important feature deduced from a parametric analysis is that equation [21] gives sometimes D values in the complex field, or when real values are given to D, the other parameters (t and I for instance) have to be changed at the same time. That is equation [21] has some mathematical indeterminations for particular pair of values. This may be deduced from figure 4 where for a particular association of I, D, and t values, the C_x one may result negative. In consequence, some pair of theoretical values may have a mathematical solution but without physical meaning. This makes this equation not always accurate from a physical point of view, and its results have to be carefully interpreted.

Comparison with a real trial -

There are very few results in the literature reporting chloride profiles before and after an electrochemical extraction treatment.

Specially for the case of initial constant chloride concentration, only one reference by Tritthart (10) has been found. His results are shown in figure 5 for the total chloride content and that in the pore solution respectively. He applied a constant current of $20A/m^2$ during a total of 25 days, to cylindrical paste specimens of 5 cm in thickness. After the trial, slices have been cut and concentration profiles established. On the figure the values of D calculated applying equation [21] are given for some points.

The values of D obtained seem to vary with the distance and time. They are also surprisingly similar the calculated from the total chloride content and those from the pore solution. These results have to be taken with precaution until more experimental results are analyzed, due to the aforementioned mathematical indeterminations that equation [21] exhibits.

Another possibility is that Tritthardt profiles were missinterpreted by this author, due to his indications about the position of anode and cathode chamber were contradictory. However, for the sake of present paper, it seems enough to have realized that results from equation [21] need a careful consideration, after being calculated.

MATHEMATICAL SOLUTION FOR CHLORIDE CONCENTRATION FOLLOWING THE ERROR FUNCTION TREND

The solution of this case was not found in the literature and, therefore, had to be solved numerically by the authors by means of a computer program specially developed using finite differences (classical implicit methods).Only potentiostatic operation is considered.

It was assumed that the chloride entrance has been produced following traditional solution of second Fick's law, arriving the chloride profile after a certain time t_i to the known (11) expression:

$$C_x=C_s\left(1-erf\frac{x}{2\sqrt{D_{(dif)}t_n}}\right) \qquad [13]$$

analytical solution of [14] for the conditions:

$$C_x(x,0) = 0 \qquad x>0$$

$$C_x(0,t) = C_s \qquad t>0$$
$$C_x(x \to \infty, t) = 0$$

The time t_n means that the time is not more a variable but it is a fixed value: that of the lifetime of the structure at the moment of the trial.

As soon as D(dif) is calculated from the real chloride profile, it is considered that the extraction process will follow:

$$\frac{\partial C}{\partial t} = D_{(mig)} \frac{\partial^2 C}{\partial x^2} \qquad [22]$$

D(mig) calculated from D(dif) following eq.[12].

Also it is assumed that Cl^- is oxidized to Cl_2 at the anode and, therefore, in the boundary x=0, c=0, that is, it exists as a discontinuity between the initial and the boundary conditions.

In order to solve equation [22], the initial condition considered was:

$$C_x(x,0) = C_s\left(1 - erf\frac{x}{2\sqrt{Dt_n}}\right) \qquad x>0$$

and the boundary conditions:

$$C_x(0,t) = 0 \qquad t>0$$
$$C_x(x \to \infty, t) = 0 \qquad t>0$$

Figure 6a depicts chloride profiles along the treatment of an example in which the values selected were D_{mig}= 800 cm^2/sec (D_{dif}=$1x10^{-8}$ cm^2/sec) and ΔE= 20v and 6b depicts the same example but assuming an applied ΔE= 60V (D(dif)= 0.3 x 10^{-8} cm^2/sec).

It can be deduced that, in the first case, 6 days are needed to deplete the chloride concentration to a value below 0.05%, while in the second case only 3 days would be enough.

Comparison with real trials -

As mentioned, only very few references are found in the literature, in spite that a project has been developed under SHRP (USA) sponsorship. The only reference found at the time of writting this paper, in which chloride profiles are given before and after the treatment is due to Elsener (12) (see figure 7). He reported a trial in a bridge applying 36 V during 8 weeks.

From the highest initial profile reported in figure 7, an approximate D(dif) value of 2,2x10^{-8} cm^2/sec has been deduced and a C_s

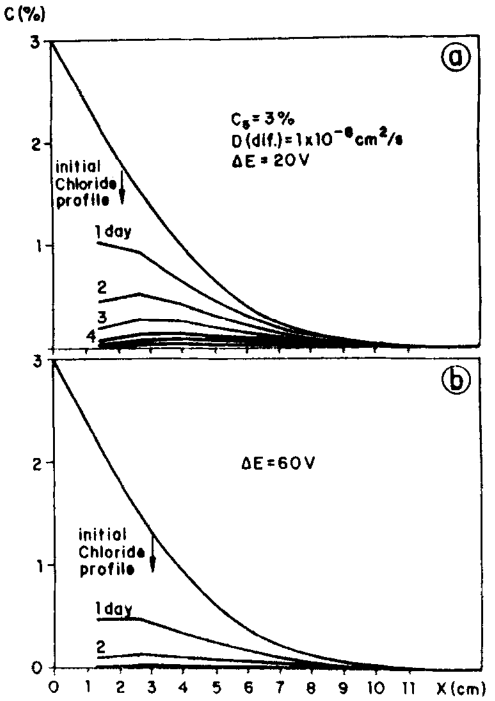

Figure 6. Calculated chloride profiles of a theoretical case in which the diffusivity of the penetration process was assumed to be 1x10^{-8} cm^2/sec, the C_s of 3% and the treatment applied of ΔE of 20 V (a) or 60 V (b).

of about 2%. Applying equation [12] to this profile, a D(mig) of 40x36x2,3= 3168 cm^2/sec is obtained, from which the profile after 4 weeks of treatment (that of the full circles in figure 7) should be modelled. However, using this D(mig)= 3168 cm^2/sec in the computer program developed only 4 days of treatment would be enough to remove all the chlorides (final concentration less than 0.01%). This period is significantly shorter than that reported by Elsener.

This disagreement may be due to the following reasons:

1) Mainly free chlorides are those removed and therefore the combined chloride remain much longer, being those detected after completion of the trial.

2) The diffusion coefficient in the extraction process is smaller (and perhaps not constant) than that of the penetration process and therefore, D(mig) could not be deduced from the initial chloride profile, that is by means of equation [12].

3) The chloride penetration has not followed equation [13].

If the first reason is operating, it would lead to the conclusion that what has to be measured is the chloride concentration in the pore solution and not the total chloride content. Whether the combined chloride are then released is a matter of controversy and

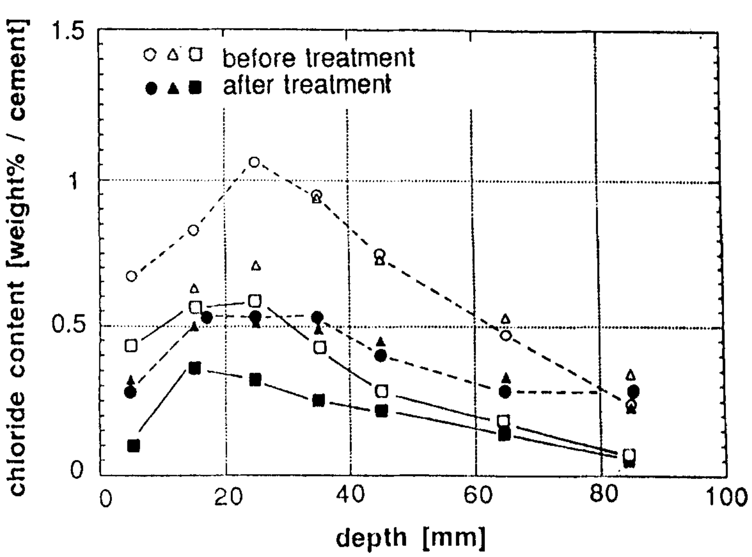

Figure 7. Chloride profiles before and after treatment of a bridge deck after Elsener (12) (reproduced with permission).

much experimentation is still needed on this point. However, what would be relevant for present discussion is the fact that only free and not total chlorides would have to be considered.

If argument 2) is the correct one, D of extraction cannot be calculated from equation [12] and, therefore, it is necessary to make the treatment in two steps: 1) the first of only few days in order to calculate the D(mig) by fitting the experimental chloride profile to the theoretical equation, and 2) as soon as the real D(mig) is obtained, prediction of the duration of the rest of the treatment would be feasible.

Applying this way of operation to the example of figure 7, the D(mig) so obtained would be two orders of magnitude smaller, that is of 31,68 cm^2/sec, which means a D(dif) of $2,2x10^{-10}$ cm^2/sec.

Finally, if argument 3) is true, that means that other boundary conditions should have been introduced. This way will be treated in a further paper.

Summarizing, either the final chloride profiles correspond to the combined chlorides, or the diffusivity of the chlorides results much smaller during the desorption process, or other Fickian expression have to be tried. Experimental confirmation of all aspects are needed. In any case, mathematical modelling is feasible.

CONCLUSIONS

1) Mathematical modelling of electrochemical chloride extraction can be undertaken by following classic electrochemical principles. Thus, the movement of chlorides during extraction may be modelled by means of Nernst-Planck equation, specially applied to the boundary conditions of a desorption process.

2) For the case of a constant chloride concentration inside the concrete, mathematical solutions are given in the literature for potentiostatic and galvanostatic operation.

a) the concentration gradient along the experiment in potentiostatic conditions is modelled by:

$$C_x = C_i \, erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

b) and for galvanostatic operation:

$$C_x = Ci - \frac{I t_{cl}}{nFAD}\left[2\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \exp\left(-\frac{x^2}{4Dt}\right) - x \, erfc\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

3) When the chlorides have penetrated from outside following a non-stationary process, a computer program using finite differences has been developed. This program has shown that it is feasible to calculate the duration of the electrochemical treatment either: a) from the value of the Diffusion Coefficient of the intrusion process or, b) from an inital practical trial in order to find out the real diffusivity governing the process.

ACKNOWDLEGEMENTS

The authors are grateful to the Formation Department of the Mining Engineering Faculty of Madrid, for allowing J.M. Diez to collaborate in this research. They would like also to thank J.Rodriguez, a student of Mechanical Engineering of Comillas University of Madrid, for his collaboration in the mathematical solution of constant initial chloride content.

REFERENCES

(1) D.R. LANKARD et al - "Neutralization of chloride in concrete" - Batelle Columbus Laboratories U.S. Dpt. of Transportation - FHWA - National Technical Information Service: Washington DC (1975) FHWA-RD-76-60, PB-255309.

(2) A.A. HACHEMI, M. MURAT, J.C. CUBAUD - "Recherche sur l'acceleration de la corrosion des aceiers dans le beton armé - Etude électrochimique théorique et éxperimentale" - Revue des Matèriaux de Construction nº 700 (1975) pp149-155.

(3) O.E. GJØRV and Ø. VENNESLAND - "Diffusion of chloride ions from seawater into Concrete" - Cement and Concrete Research, vol.9, pp 229-238 (1979).

(4) C. ANDRADE - "Calculation of chloride diffusion coefficients on concrete from ionic migration measurements". Cement and Concrete Res. vol. 23 pp.724-742 (1993).

(5) C. ANDRADE, M.A. SANJUAN - "Experimental procedure for the calculation of chloride diffusion coefficients in concrete from migration tests" - Advances in Cement Research (accepted for publication).

(6) C. ANDRADE, M.A. SANJUAN, A. RECUERO, O. RIO - "Calculation of chloride diffusivity in concrete from migration experiments in non-steady state conditions" - Cement and Concrete Research 24(7), 1214-1228 (1994).

(7) M. POURBAIX - "Lectures on Electrochemical Corrosion". Ed. Cebelcor - Plenum Press - New York (1973).
(8) J.O'M. BOCKRIS, A.K.N. REDDY - Modern Electrochemistry - Plenum Press Ed. New York (1974).
(9) A.J. BARD, L.R. FAULKNER - Electrochemical Methods. Fundamentals and Applications - Jon Wiley & Sons Ed., (1980).
(10) J. TRITTHART, K. PETTERSON, B. SORENSEN - "Electrochemical Removal of chloride from hardened cement paste" - Cement and Concrete Research 23(5), 1095-1104 (1993).
(11) J. CRANK - The Mathematics of Diffusion, Ed. Oxford University (1975).
(12) B. ELSENER, M. MOLINA, H. BÖHNI - "The electrochemical removal of chlorides from reinforced concrete" - Corrosion Science, vol. 35, nº 5-8, pp 1563-1570 (1993).