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# Electrochemical removal of chlorides Modelling of the extraction, resulting profiles and determination of the efficient time of treatment

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## Abstract

Due to the increase in the hydroxyl ion concentration generated as a consequence of the cathodic reaction of water electrolysis, the diffusion coefficient of chloride ions decreases during chloride extraction experiments. In a previous work carried out by the authors, an empirical equation to model this decrease in the diffusion coefficient as the treatment proceeds was given. Based on this equation, mathematical modelling of the extraction is carried out in this paper. This modelling allows the calculation of the time needed to achieve a particular percentage of chloride extraction as a function of the electrical charge passed, as well as the remaining chloride profile in the concrete. Numerical examples applied to the case in which chlorides were homogeneously distributed in the specimens are given to illustrate the modelling. These are also applied to experimental results previously published by other authors, finding a good accordance.

*Keywords:* Desalinisation; Mathematical modelling; Electrochemical removal of chlorides; Diffusion coefficient

## 1. Introduction

Since chloride removal in concrete was first investigated [1,2], the application of electrical fields to concrete, as non-destructive repair methods, has been increasingly used [3–6]. Therefore, a great interest in the understanding of mechanisms involved in the electrochemical process has arisen. Although the main processes developed during the application of electrical fields to concrete structures are at present better known [3–8], mathematical modelling of the phenomenon is not completely developed, in spite of the fact that models have been proposed. For example, a recent model [9] has been published on the basis that electrochemical removal is dominated by the rate of release of bound chloride.

In order to understand the phenomena developing during electrochemical treatments and consequently, to be able to model it, it is necessary to consider that transference numbers are one of the key parameters in the description of a system in which electrolytic transport of current is involved. The transference numbers determine the amount of current carried by the species of interest, and therefore give their rate of transport. In the literature, references to transference numbers, in association with the efficiency of electrochemical chloride extraction, can be found [3,9–13]. However, their evolution is not considered in the modelling of the electrochemical extraction. In a recent paper, Sa'id-Shawqi et al. [14] modelled the extraction from chloride transport numbers, but assuming that the chloride ion diffusion coefficient remained constant during desalination.

In the present paper, as a continuation of the previous work developed by the authors on the application of electrical fields to concrete, mathematical modelling of the processes occurring during the electrochemical chloride extraction is undertaken. The modelling is based on experimental trials previously reported in Ref. [15]. It takes into account the fact that the efficiency of the technique (with regards to the percentage of extraction) and also the chloride transference numbers, decrease as the treatment proceeds. This is modelled as a progressive

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decrease in the diffusion coefficient. The model has been applied to results of Bertolini et al. [16], and the findings exhibit good correlation.

### *1.1. Development of the mathematical model*

The development of the mathematical model is based on the previous work by the authors [17–19]. There, it was established for practical uses that it can be used an analogy of treatment between migration and diffusion under non-steady-state conditions. This analogy is based on considering a "migration coefficient," $D_{\mathrm{mig}}$, which enables any known solution of a diffusion problem to be applied to a migration experiment.

This analogy with diffusion tests has already been used in the calculation of chloride diffusion coefficients during electrochemical extraction [19], when either chloride is present in a constant concentration in concrete, or when there is a chloride profile as a result of the exposure of concrete to a contaminated environment. However, in the previous work [19], model predictions did not completely fit experimental data. This led to the conclusion that the diffusion coefficient during the extraction experiment had to be smaller than the value derived from the penetration period (profile fitted) what now is attributed [15] to the fact that the diffusion coefficient does not comply with the assumed constancy during the treatment.

The experimentation has shown that the most important factor to consider is that the efficiency in chloride extraction reduces as the treatment proceeds [15,20,21]. The best way to represent this is by means of the transference number of chlorides. Decrease in accumulative transference numbers (average from the beginning of the test until the moment of calculation) follows a potential trend that has been mainly attributed to the $\mathrm{OH}^-$ generation (as a result of the cathodic reaction of water electrolysis) which preferentially carry the current due to their higher mobility [15,21]. Therefore, it can be justified that the "extraction" diffusion coefficient decreases during the extraction period as a consequence of the decrease in the chloride transference number. In addition, in a similar manner to the decrease of transference numbers, chloride diffusion coefficient during the extraction depends on the circulated charge during the test [15]. In this way, a mathematical expression of general application was derived from experimental work in which chlorides were homogeneously distributed through the specimen and using external electrodes [15]. This equation [Eq. (1)] allows the calculation of the diffusion coefficient at every specified time for each experiment:

$$D_{\mathrm{ext}} = \frac{D_{0(\mathrm{mig})}}{\mathrm{e}^{[5\mathrm{E}-7(Q/m^2)]}} \tag{1}$$

where $D_{\mathrm{ext}}$ is the accumulative diffusion coefficient of chlorides during the extraction for a settled amount of electrical charge density passed; $D_{0(\mathrm{mig})}$ is the initial diffusion coefficient of chlorides corrected to take into account the acceleration of the electrical field applied [18]; $Q$ is the electrical charge passed (coulombs).

With regard to this expression and taking into account that during the removal treatment, diffusion coefficient of chlorides is not constant, it arises the need to properly define conditions before calculation. Therefore, in analogy to the nomenclature established for transference numbers [22], diffusion coefficients used in present study are the accumulative ones, as long as the coefficients calculated for a specific time (electrical charge) are the averaged value from the start of the test until the moment of calculation.

The expression given in Eq. (1) can be implemented in any of the equations used for describing the extraction process.

### *1.2. Application of the mathematical model*

The approach is applied here to the case where the chlorides are added to the water and therefore, are homogeneously distributed in the sample. The process is as follows.

1. Determination or assumption of an "initial" diffusion coefficient of chlorides through the matrix ($D_0$).
2. Calculation of the corresponding initial $D_{0(\mathrm{mig})}$ taking into account the specific characteristics of the electrochemical treatment (electrical potential drop and geometry of the specimen), according to Eq. (2) [23].

   $$D_{0(\mathrm{mig})} = \frac{zF}{RT} D_0 \frac{\Delta\phi}{2\ln(2l)} \tag{2}$$

   where $\Delta\phi$ is the voltage difference applied (V) and $2l$ is the thickness of the specimen or of the cover (cm).
3. For each time period, calculation of the decrease in the migration coefficient due to the passage of current and the consequent decrease in transference number, in accordance with Eq. (1).

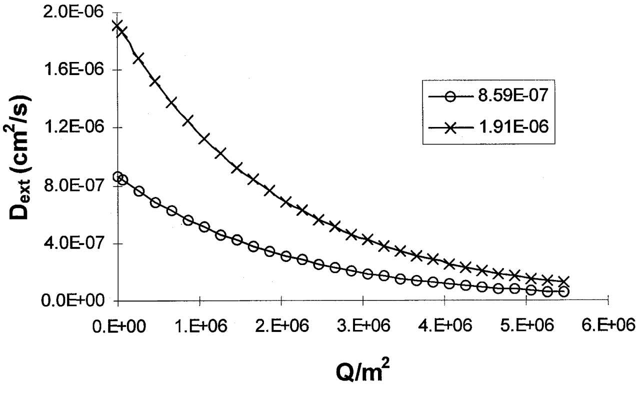

Fig. 1. Evolution of $D_{\mathrm{ext}}$ as the experiment proceeds for two different current densities applied to the same concrete ($D_0$ = 0.77E − 8 cm²/s).

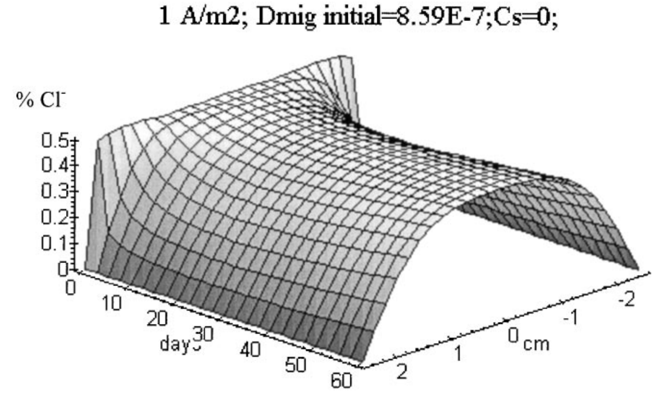

Fig. 2. Predicted chloride profiles in the specimen at a current density of 1 A/m$^2$.

4. Calculation of the chloride profiles during the extraction assuming an initial condition (profile or homogeneous distribution of chlorides).

## 2. Numerical examples on concrete having a homogeneous chloride distribution

### 2.1. Example I: Theoretical calculation

(1) Considering a concrete specimen of 10 × 10 × 5 cm, homogeneously contaminated with chlorides (initial concentration, Co = 0.5% by weight of concrete) and a resistivity of about 16,000 Ω cm, it can be assumed an initial diffusion coefficient for chlorides ($D_0$) of 0.77E−8 cm$^2$/s in accordance with the modified Nernst–Einstein equation [4].

(2) Calculation of $D_{0(\mathrm{mig})}$: If a current density of 1 A/m$^2$ is applied, and taking into account the value of the resistivity, a voltage drop of 9 V is required. In these conditions, the initial $D_{0(\mathrm{mig})}$ of chlorides in the extraction will be of 8.59E−7 cm$^2$/s [23]. If the experiment is going to be run at 2 A/m$^2$, a voltage of approximately 20 V will be needed. Therefore, in this case the initial $D_{0(\mathrm{mig})}$ will be of 1.91E−6 cm$^2$/s.

(3) According to Eq. (1), the extraction diffusion coefficient of chlorides will decrease as the test proceeds. This is shown for this particular example in Fig. 1. It is important to point out that for the same concrete, depending on the experimental conditions of the desalination, the diffusion coefficient of the extraction process will be different. As can be seen in Fig 1, there is a comparatively greater decrease in diffusion coefficients when the initial diffusion coefficients are high.

(4) Fitting the experimental profiles to the corresponding diffusion equation: Present example deals with an initial chloride concentration uniformly distributed in the specimen [14,15] and external electrodes. The resulting profile will have a maximum in the centre of the specimen due to a "push-and-pull" effect at the end zones [15]. Therefore, a diffusion equation of a desorption process of a compound initially homogeneously distributed in a membrane of thickness $2l$ is selected for this case. The surface concentration to both sides of the membrane has been assumed to be constant. The solution is given by Eq. (3) [24].

$$\frac{C-C_0}{C_1-C_0}=1-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{-1^n}{2n+1}\cdot\exp[-D_{\mathrm{ext}}(2n+1)^2\pi^2t/4l^2]\cos\frac{(2n+1)\pi x}{2l} \tag{3}$$

where $C(x,t)$ is the chloride concentration at depth $x$ and a time $t$ (%); $C_0$ is the initial chloride concentration in the specimen (%); $C_1$ is the surfaces' chloride concentration (%); $x$ is the depth in the specimen (cm) ($-l < x < l$).

Thus, the modelling of the extraction process according to this equation has to consider for each time the corresponding charge density that has passed and consequently the calculated extraction diffusion coefficient ($D_{\mathrm{ext}}$). For these calculations, it has been assumed that

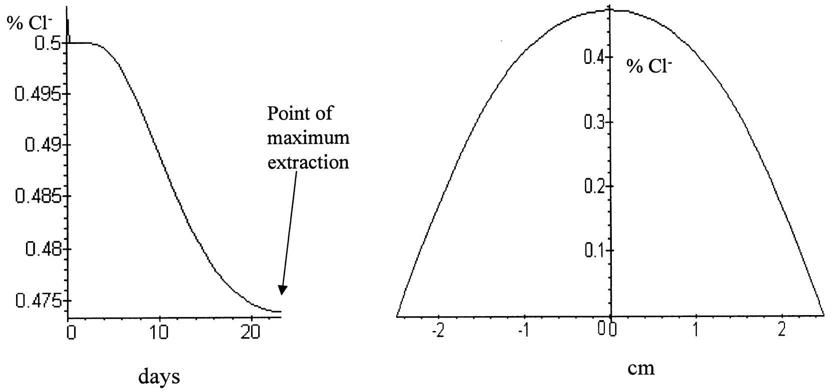

Fig. 3. (a) Evolution of the predicted concentration of chlorides in the medium point of the specimen (cm = 0) at a current density of 1 A/m$^2$. (b) Corresponding profile when the maximum extraction is reached (23 days).

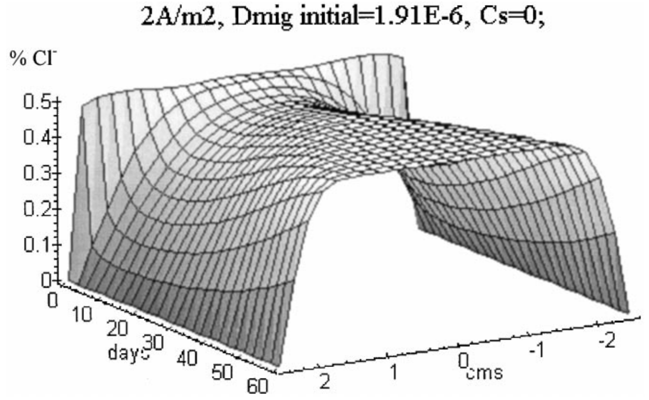

Fig. 4. Predicted chloride profiles in the specimen at a current density of 2 A/m$^2$.

surface concentration to both sides of specimen is equal to zero (in order to illustrate a more favourable extraction case). With these assumptions, the profiles of chlorides that are obtained for current densities of 1 and 2 A/m$^2$ are shown in Figs. 2–5.

In Fig. 2, a three-dimensional plot shows the concentration of chlorides at every depth of the specimen from 0 to 60 days.

In Fig. 2, it can be seen that there is a specific time where the extraction reaches a maximum, that is to say, concentration of chlorides in the specimen reaches a minimum, being a later increase in chloride concentration.

This minimum chloride concentration at a specific duration of the process is attributed to the fact that in this treatment as previously commented, accumulative diffusion coefficients are being used. The mathematical appearance of the minimum is a consequence of the fact that there is a point in which the accumulative extraction diffusion coefficient has decreased so much that an additional increase in the time of the treatment does not imply further desalinisation, since the global coefficient becomes smaller. Therefore, the exact point where the minimum appears gives very important information. Beyond this point, further treatment time will not have any practical influence on extraction. Therefore, this modelling reproduces the actual behaviour until maximum extraction is reached. This will give the optimum treatment time.

In this case of a current density applied of 1 A/m$^2$, the minimum in chloride concentration takes place after approximately 23 days of treatment. This can be clearly seen in Fig. 3, where for a specific depth of the specimen (in this case, the medium point, where concentration of chlorides is the highest one; cm = 0) the evolution in the predicted concentration is shown (Fig. 3a). In Fig. 3b. the resulting profile corresponding to this time is given.

In the case of a current density applied of 2 A/m$^2$, following the same presentation than in the previous case, Fig. 4 shows the three-dimensional plot of calculated profiles at different times.

As it occurred in the case of a current density of 1 A/m$^2$ applied, there is a minimum in the chloride concentration, that in this case takes place after approximately 11 days of treatment, as can be seen in Fig. 5a. For this time, resulting profile is shown in Fig. 5b.

Another interesting point derived from this modelling is that it is not possible to reach complete desalinisation. For each system, a certain limit of extraction cannot be exceeded. Beyond this point, chloride transference number is so low that chlorides do not take any part in carrying the current.

### 2.2. Example II: Application of the proposed calculations to the experimental results from Bertolini et al. [16]

The model has been also applied to the experimental data reported by Bertolini et al. [16] where cathodic

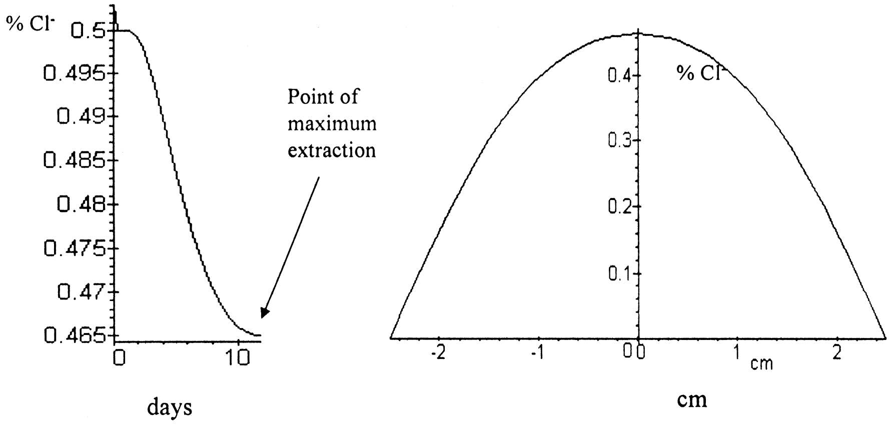

Fig. 5. (a) Evolution of the predicted concentration of chlorides in the medium point of the specimen (cm = 0) at a current density of 2 A/m$^2$. (b) Corresponding profile when the maximum extraction is reached (11 days).

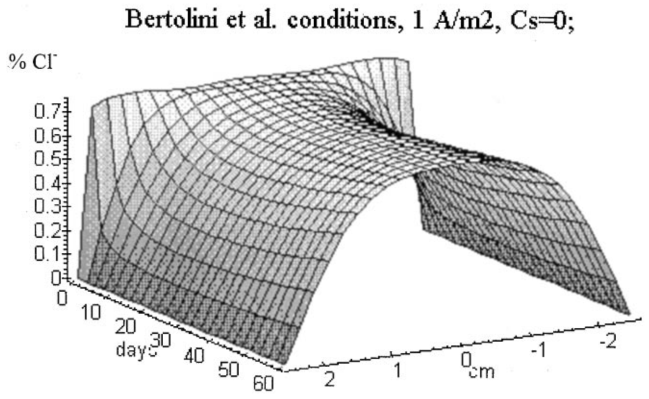

Fig. 6. Theoretical chloride profiles at an applied current density of 1 A/m$^2$ from experimental work by Bertolini et al. [16].

current densities of 1 and 5 A/m$^2$ were applied (during 4 and 8 weeks) to prism specimens of Portland cement paste cast at a water/cement ratio of 0.35 with an estimated initial chloride concentration respect to the total weight of sample of 0.74. Considering the geometry of the specimens and the paste resistivity, a potential drop of 3.5 and 20 V has been calculated as necessary to reach 1 and 5 A/m$^2$, respectively. For $D_0$, a value of 2E−8 cm$^2$/s has been assumed as a rough extrapolation of values that the same authors gave for OPC pastes [25] at a water/cement ratio of 0.35. Using these data, initial $D_{0(\mathrm{mig})}$ of 8.61E−7 and 4.92E−6 cm$^2$/s, respectively, have been obtained.

Modelling of the extraction process (assuming surface concentration on both sides of the specimen as equal to zero) is shown in Figs. 6–9.

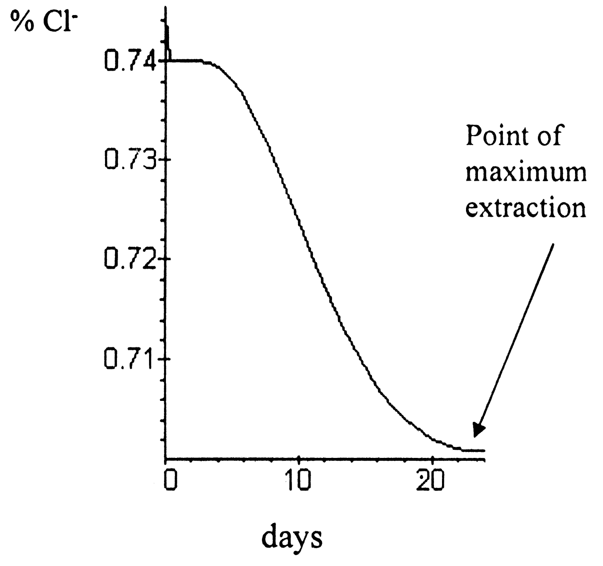

Fig. 7. Evolution of the predicted concentration of chlorides in the medium point of the specimen (cm = 0) at a current density of 1 A/m$^2$ from experimental work by Bertolini et al. [16].

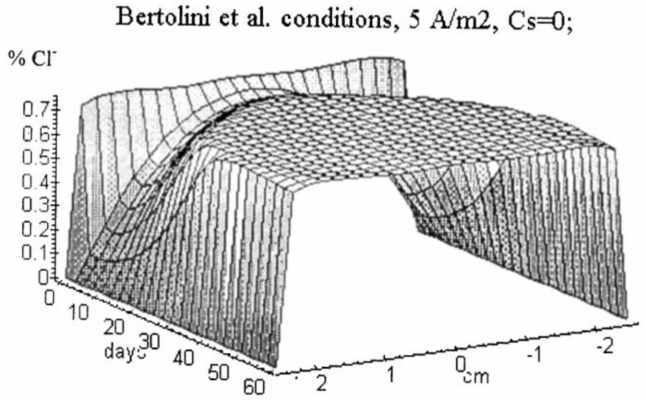

Fig. 8. Theoretical chloride profiles at an applied current density of 5 A/m$^2$ from experimental work by Bertolini et al. [16].

In Fig. 6, the three-dimensional plot of calculated profiles at different times for an applied current density of 1 A/m$^2$ is shown. From Fig. 6, it can be deduced that the desalination level under this conditions is not very high when the point at which minimum concentration of chlorides in the specimen is reached, which is achieved at approximately 23 days, as can be seen in Fig. 7.

Modelling for an applied current density of 5 A/m$^2$ is presented in Figs. 8 and 9, where it can be seen that the point of maximum desalination is reached much sooner than in the case of current density of 1 A/m$^2$, at approximately 5 days.

This implies that in the case of a current density of 1 A/m$^2$ applied over 4 weeks, experimental profiles should be similar to the theoretical profile within this period. The

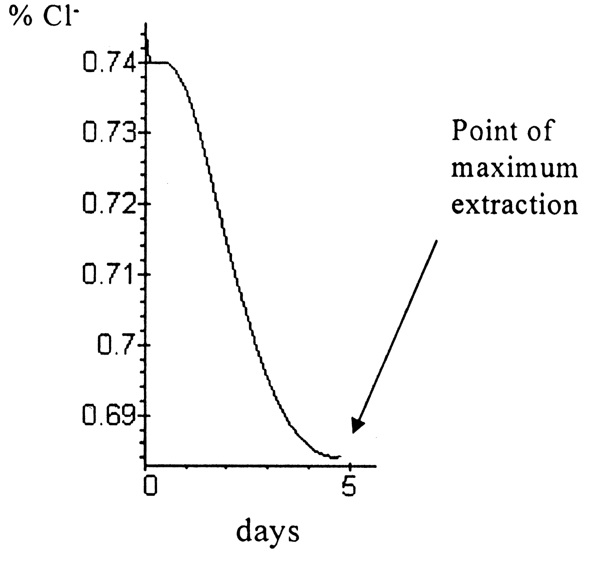

Fig. 9. Evolution of the predicted concentration of chlorides in the medium point of the specimen (cm = 0) at a current density of 5 A/m$^2$ from experimental work by Bertolini et al. [16].

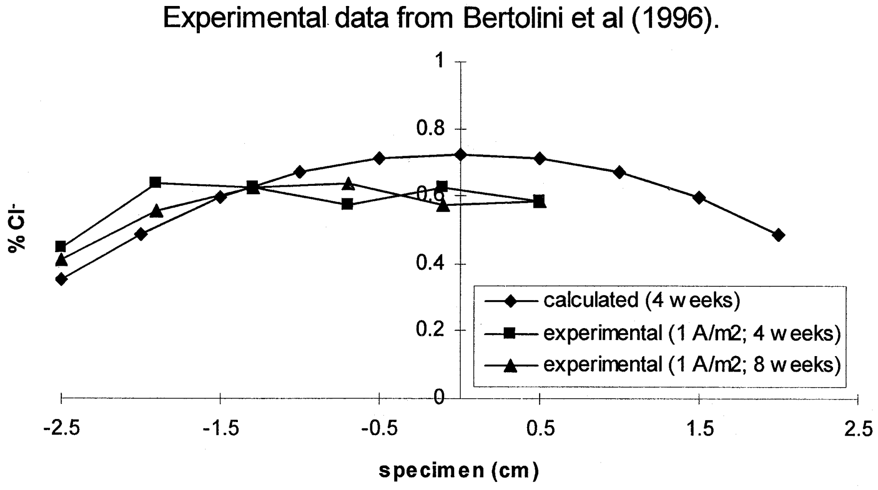

Fig. 10. Comparison between experimental and predicted profiles (current density = 1 A/m$^2$).

same current density applied over 8 weeks should be very similar to the extraction level at 4 weeks, since this is quite close to the maximum extraction. Comparison between experimental and predicted profiles for a current density of 1 A/m$^2$ can be found in Fig. 10.

It can be seen from Fig. 10 that the correlation between the experimental and predicted profiles is quite good. In the case of an applied current density of 5 A/m$^2$, 4 and 8 weeks are beyond the maximum percentage of extraction, which according to the previous discussion, implies that experimental profiles must be fitted to the theoretical ones corresponding to the maximum extraction (5 days). Comparison between experimental and predicted profiles can be found in Fig. 11, where again the correlation is satisfactory.

## 3. Conclusions

The study presented here, based on previous experimental results, made it possible to draw up the following conclusions.

(1) The calculation or assumption of an initial diffusion coefficient, taking into account the increase in its value due to the electrical field and its decrease during the treatment, has allowed to model the electrochemical chloride extraction in concrete.

(2) The decrease in the chloride transference number of chloride during the desalination due to the OH$^-$ generated by the cathodic reaction, and the consequent decrease in the efficiency of the treatment,

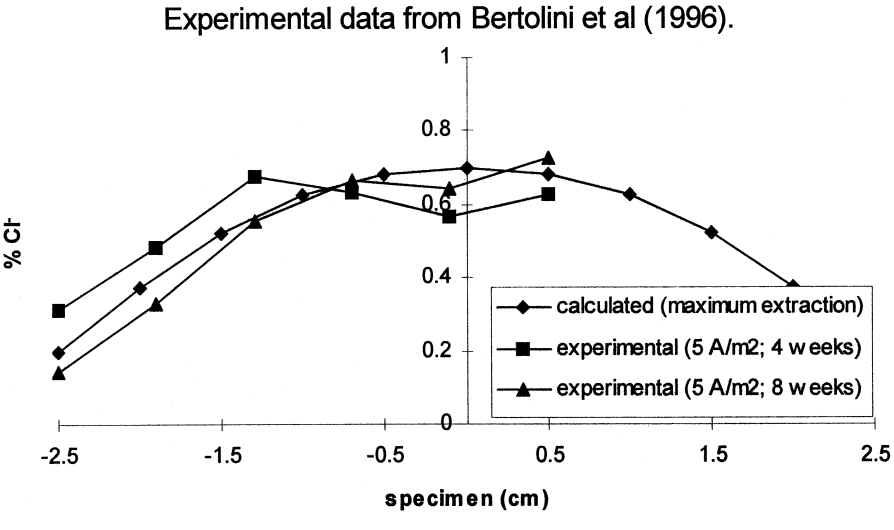

Fig. 11. Comparison between experimental and predicted profiles (current density = 5 A/m$^2$).

implies that there is a limit in the amount of extraction for each structure; it is impossible to reach complete desalinisation, at least in one step, what has been taken into account in the model.

(3) Prediction of the evolution of chloride profiles during the treatment has been made as follows. (a) Determination of the initial diffusion coefficient of chlorides ($D_0$). (b) Calculation of the corresponding $D_{0(\mathrm{mig})}$ as a function of the electrochemical removal conditions. (c) Calculation of the decrease in this migration coefficient due to the passage of current. (d) Using the previous coefficient, calculation for each time of the profile of the remaining chlorides along the specimen by means of the corresponding natural diffusion equation.

(4) In addition to the remaining chloride concentration profiles, other important output of this model is the data of the optimum time of extraction, beyond which, no more extraction can be achieved. The possibility of knowing this point has very important economic implications, as it represents the point to stop the treatment.

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