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Phenomenological mass-balance-based model of migration tests in stationary conditions
Application to non-steady-state tests

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Abstract

In order to understand the phenomena that take place during a migration test, and to obtain a complete picture of the system through the pursuit of the transference numbers, a phenomenological mass-balance-based model of the evolution of all ionic species, has been developed. The model has been built on a series of steady-state migration tests and has been experimentally validated. Afterwards, it has been applied to migration tests in non-stationary conditions, and the resulting deductions have also been checked with experimental results. This has allowed the development of a new simplified way to determine the non-steady-state diffusion coefficients, D_{ns}, just from the registration of the current intensity circulating and the analysis of the surface concentration, C_s, after the test. In addition, the possibility of the tabulation of the different C_s for different external chloride concentrations and the application of different "binding factors" for each kind of binder is posed, which will allow the calculation of the D_{ns} from a simple migration test of the AASHTO type (ASTM C1202-91). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Concrete; Chloride diffusion coefficients; Migration tests; Transference numbers; Phenomenological model

1. Introduction

When an electrical field is applied to an electrolyte, the current in the solution is carried by all the ions. The conductivity of the solution is the sum of the contribution of every species electrically charged. This contribution depends on their concentration, charge, and mobility [1]. The expression of the transference number of a species is given by Eq. (1):

$$t_i = \frac{z_i c_i \Lambda_i}{\sum z_i c_i \Lambda_i} \tag{1}$$

where t_i = transference number of the species i, c_i = concentration of the species i, and Λ_i = equivalent conductivity of the species i.

Therefore, the amount of current transported by each of the species of the pore concrete solution will depend on their transference number. Therefore, in order to understand the phenomena developing during an electrochemical treatment 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 any system in which electrolytic transport of current is involved [2]. The transference numbers determine the amount of current carried by the species of interest, and therefore give their rate of transport.

According to its definition, the calculation of chloride transference numbers can also be done from current intensity circulating through the specimen and from the flux of chlorides resulting from this circulation Eq. (2) [2]

$$t_{Cl} = \frac{zFJ}{i} \tag{2}$$

where t_{Cl} = chloride transference number, F = Faraday constant (C/eq), J = flux of chlorides (mol/cm^2 s), and i = total current density (A/cm^2).

Transference numbers depend on the concentration of every charged species in the solution. This means that in the case of concrete during a migration test, it is necessary to take into account every species involved during the experi-

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Table 1
Chemical analysis of the cement used

L.I. (%)	I.R. (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Free CaO (%)	Cl^- (%)	Na_2O (%)	K_2O (%)
3.45	1.97	19.37	6.12	3.13	62.86	1.78	3.23	1.28	0.013	0.18	1.00

Table 2
Dosage of the concrete

	Cement (kg/m^3)	Sand (kg/m^3)	Coarse aggregate (kg/m^3)	Water (kg/m^3)	Ratio (w/c)
Concrete	380	771	1177	152	0.4

ment. Therefore, not only chloride ions, but also the other ions initially present, as well as those generated from the electrodic reactions, have to be taken into account in the calculation of the transference numbers.

In the literature, references to transference numbers in association to the efficiency of electrochemical chloride extraction can be found [3–8], but in general, its evolution is not considered in modelling the electrochemical extraction. In addition, no references to a systematic study of the processes that take place during a migration experiment through the pursuit of transference numbers have been found.

In a previous work, a specific nomenclature of the different transference numbers (according to the parameters used to calculate them) was proposed [9]. According to this nomenclature, transference numbers in concrete can be defined as:

- Anodic transference numbers (t_a) — where the considered flux of chlorides is that which passed into the anodic compartment.
- Cathodic transference numbers (t_c) — where the considered flux of chlorides is that which has disappeared from the cathodic compartment.
- Differential transference numbers (t_d) — transference number calculated at a specific time that corresponds to a small interval around this time (using current intensity and flux of chlorides during each period between two consecutive taking of samples).
- Accumulative transference numbers (t_{ac}) — transference number calculated until a specific time. This is the average from the starting of the test until that moment (using current intensity and flux of chlorides averaged up to the considered moment).

According to this nomenclature, the proper definition of a transference number has to include the reference to the flux of chlorides, as well as to the period considered. In consequence, during a steady-state migration test, we can find four types of transference numbers: anodic differential (t_{ad}), cathodic differential (t_{cd}), anodic accumulative (t_{aac}), and cathodic accumulative (t_{cac}) transference numbers. The use of one or another will depend on the reasons for their calculation and the nature of the study being carried out.

As a continuation of the work in this field, and with the aim of contributing to a better understanding of the phenomena developing during a migration experiment, the authors have carried out a phenomenological mass-balance-based model of migration tests in stationary conditions. The application of this model to the non-stationary conditions has resulted in the development of a new simplified method to determine the non-steady-state diffusion coefficient, D_{ns}.

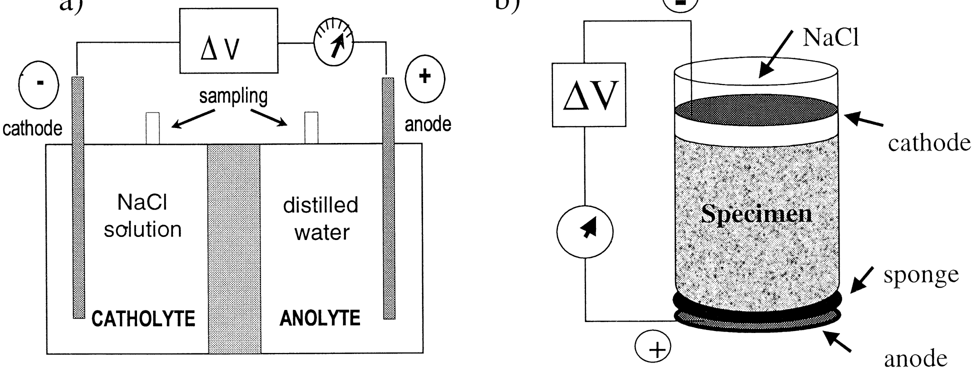

Fig. 1. Experimental devices used: (a) steady-state tests; (b) non-steady-state tests.

2. Experimental

2.1. Materials and specimens

The specimens were made of concrete (w/c = 0.4) and were cylindrical, of 75 mm diameter. They were demoulded after 24 h of being cast and cured during 28 days under water. Then, they were stored until testing time in a $Ca(OH)_2$ saturated solution.

The chemical composition of the cement, as well as the dosage of the concrete are shown in Tables 1 and 2, respectively.

2.2. Techniques and procedures

Two types of arrangements were used, in steady state and in non-steady state (see Fig. 1).

To perform the tests in steady-state conditions, the migration cell of two compartments described in Ref. [10] was used (Fig. 1a). A 10-mm-thick concrete disc was used as specimen and was introduced between the two chambers (of about 325 cm^3) where the cathode and the anode were placed. A series of experiments with different chloride concentrations in the catholyte (0.05, 0.1, 0.2, 0.5, and 1 M NaCl solutions) were performed. Distilled water was introduced in the compartment where the anode was located (anolyte) in all the cases. The voltage applied was 12 V and the actual voltage drop across the concrete disc was monitored by introducing two calomel reference electrodes in both chambers [10]. Two corrugated rebars of 10 cm in length and 0.6 cm in diameter were used as electrodes. Periodically during the experiment, pH evolution (a pH electrode valid in the range 0–14 and a Crison pH-meter were used for the measurements) and Cl^- concentration in both compartments were monitored.

For the tests in non-steady-state conditions, an arrangement of "ponding" type was used (Fig. 1b) with a voltage of 12 V DC applied, and steel electrodes. Different series of non-steady-state migration tests were performed. The variables studied were: (a) The concentration of chlorides in the catholyte: 0.05, 0.1, 0.5, and 1 M NaCl solutions in tests of 3 weeks of duration and depth of the specimen of 150 mm. (b) Duration of the test: 0.5 M NaCl during 1, 2, 3, and 4 weeks and depth of the specimen of 150 mm. (c) Depth of the specimen: specimens of 72-, 115-, and 150-mm depth with a 0.5-M solution of NaCl during 1 week. At the end of each experiment, the specimen was cut in slices (about 5–10 mm thick), which were analysed by X-ray fluorescence in order to obtain the total amount of chlorides.

3. Results

3.1. Steady-state experiments

Fig. 2a–b shows the evolution of the amount of chloride ions in both compartments for the different concentrations initially added to the catholyte.

In Fig. 2a, it can be observed that the amount of chlorides passing to the anolyte evolves in three stages, previously identified during a steady-state migration test [9]. Initially, there is a period in which the amount of chlorides that passes to the anolyte is negligible. Its duration corresponds to the "time lag." Afterwards, there is a steady-state period, in which the flux of chloride ions through the specimen is constant. In the last step, the amount of chlorides emerging to the anolyte starts to decrease, when comparing with the steady-state period.

As far as the catholyte chloride evolution is concerned (see Fig. 2b), the curves recorded always presented a decreasing trend.

Fig. 3 shows the differential transference numbers for chloride ions calculated from the chlorides that have reached the anolyte (t_{ad}(Cl)) (Fig. 3a), and calculated from the chlorides that have left the catholyte (t_{cd}(Cl)) (Fig. 3b) in function of the charge passed in coulombs (Q).

In these pictures, it can be noticed that anodic transference numbers reach a maximum while cathodic ones, as a general trend, initially diminish progressively, to reach a stable value.

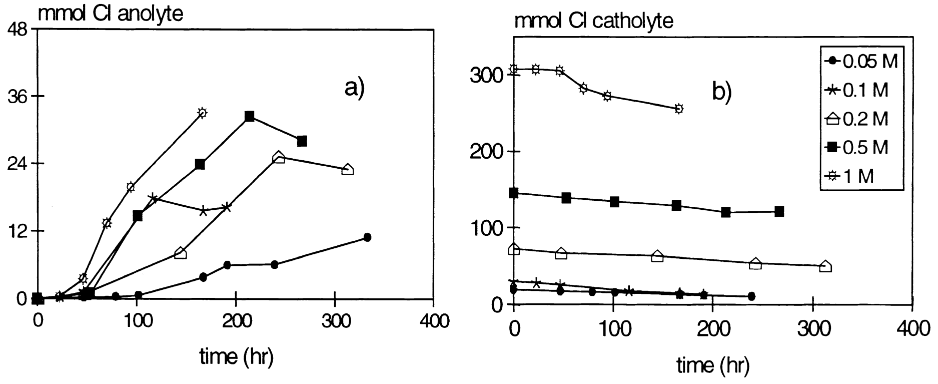

Fig. 2. (a–b) Evolution of the amount of chloride in anodic (a) and cathodic (b) compartments for different NaCl concentrations.

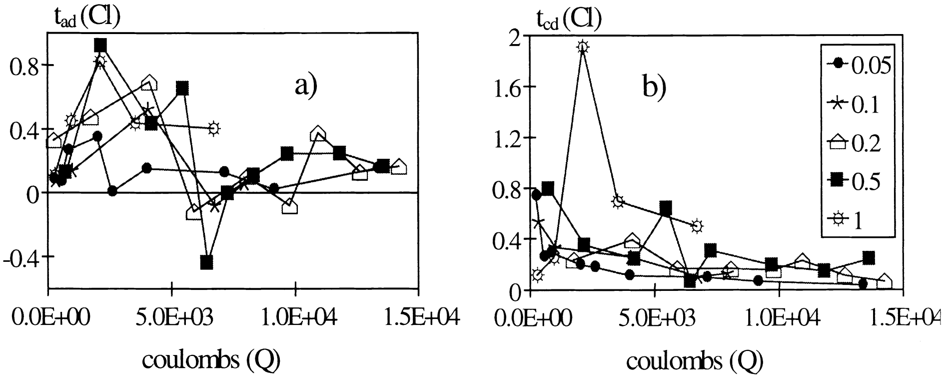

Fig. 3. Differential chloride transference numbers (t_{ad}(Cl) and t_{cd}(Cl)) in function of the charge passed (*Q*).

3.2. Non-steady-state tests

Fig. 4 shows the chloride profiles obtained after the tests for every concentration, duration, and depth of the experiment (percentage with respect of dry sample).

In Fig. 5, it can be seen the cathodic accumulative chloride transference numbers, t_{cac}(Cl) for the non-steady-state experiments, calculated at the end of the tests, in function of several parameters: Fig. 5a — initial concentration of the catholyte; Fig. 5b — duration of the test; and Fig. 5c — depth of the specimen.

In this figure, it can be seen that the fraction of current that carries the chloride ions is higher as higher is the concentration of the catholyte. As long as the duration of the test is concerned, for the periods of time tested in present study, it cannot be appreciate any dependence with the time. The depth of the specimen neither seems to influence the t_{cac}(Cl) obtained at the end of the tests (Fig. 5c).

The chloride concentration at the surface of the specimens, C_s, is shown in Fig. 6a–b, where it can be seen that this parameter increases with the concentration of the external solution. Concerning the same external concentration at different times tested, the C_s varies randomly around a certain value (for 0.5 M NaCl, around 0.35).

4. Discussion

The variability of the transference numbers is due, as previously mentioned, to their dependence on the concentration of every charged species in the solution. During a migration experiment, concentration of every species is con-

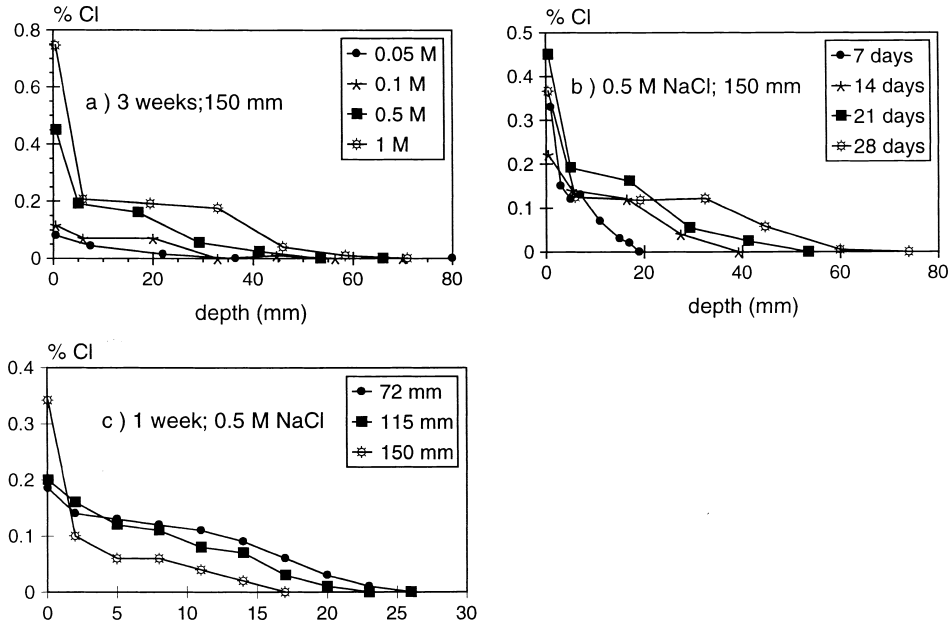

Fig. 4. Chloride profiles obtained at the end of each experiment.

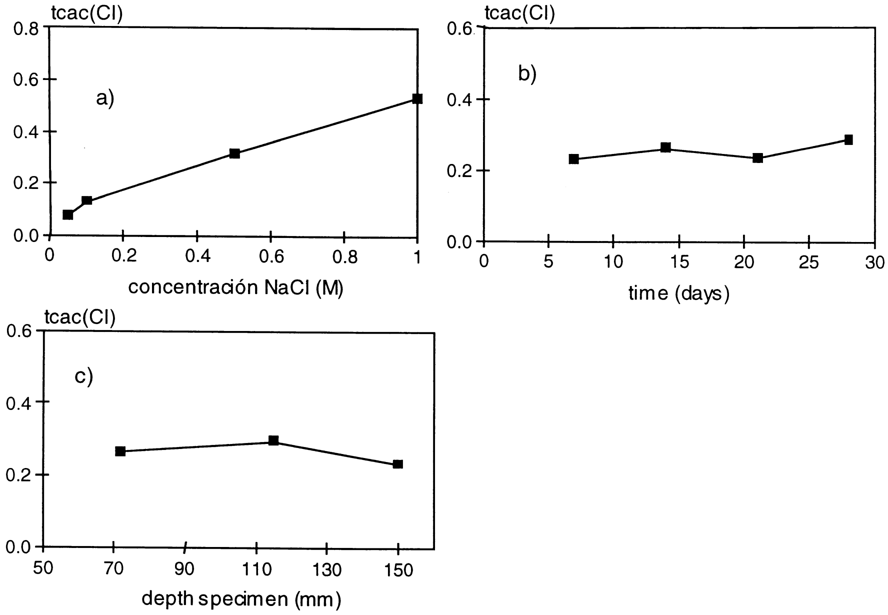

Fig. 5. t_{cac}(Cl) calculated at the end of the tests in function of: (a) initial concentration of the catholyte; (b) duration of the tests; and (c) depth of the specimen.

tinuously changing, not only because of their own movement under the action of the electrical field, but also due to the ions generated from the electrodic reactions; therefore, it is clear that transference numbers do not have to be constant.

Therefore, for the sake of the aim of present study (to find a simplified way of calculation of D_{ns}), on the one hand, it is necessary to properly define the conditions for the calculation of transference numbers, what has been previously done by the definition of a specific nomenclature [9]. On the other hand, it is necessary to systematically study the processes that take place during a migration experiment through the pursuit of the transference numbers, developing phenomenological models able to be applied to different electrochemical treatments.

4.1. Phenomenological model for quantifying transference numbers in steady-state migration tests

In order to obtain a complete picture of the steady-state migration system through transference values, a phenomenological model of the evolution of all ionic species needs to be established.

The framework considered in the development of this kind of model was the following.

- A steady-state migration test system can be modelled as being composed of three different parts (catholyte, anolyte, and specimen) sequenced in series, which can be treated independently in such a way that, in each of them, the sum of the transference numbers corresponding to every species involved is equal to the unity.
- Involved species in each compartment are of four types: (1) the initial ones; (2) those generated from the electrodic reactions; (3) those that migrate out of the compartment; and (4) those that enter the compartment through the specimen.
- Ions leached from the specimen are not taken into account due to the short duration of the tests and to the generation of hydroxyl ions and protons, in the catholyte and anolyte, respectively, in an amount much higher than those corresponding to the leached ions.

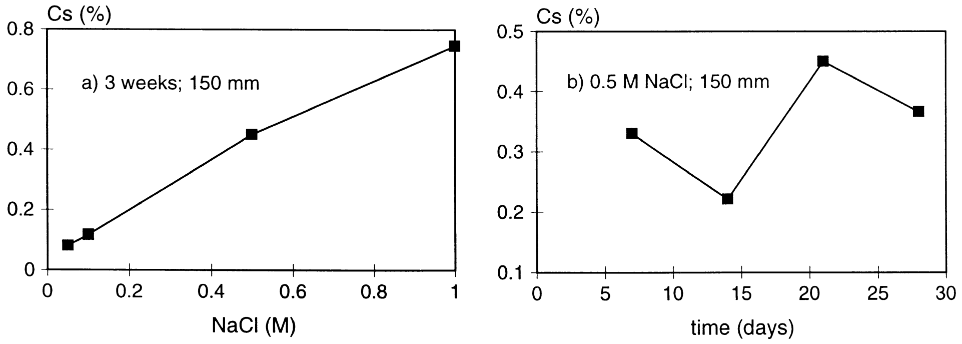

Fig. 6. (a–b) Chloride concentration at the surface of the specimens, C_s, at (a) different chloride concentrations; (b) different testing time.

The experimental validation of the model has to be done by the calculation of a key parameter that could be compared to the experimentally obtained one. For the studied system (NaCl in the catholyte and steel electrodes), the parameter chosen has been the pH of the catholyte.

Therefore, for each of the three zones (catholyte, anolyte, and concrete disc) into which the system has been divided, it is necessary to study the processes that take place. The selected parameter (catholyte pH) is then calculated through a mass balance for each interval between two consecutive samplings.

4.1.1. Zone I: cathodic compartment

The main electrodic reaction considered to take place is:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$

The reduction of oxygen has not been considered because the values of electrical potential reached in the cathode are so negative that a negligible contribution of this reaction is assumed.

Following Faraday's law and according to Eq. (3), for each 96 486 C of current that passes, the formation of one equivalent of OH^- in the catholyte takes place.

In addition to the generated OH^-, species of interest in this compartment are the Na^+ and Cl^- initially present in the catholyte solution. Therefore, the global equation of transference numbers for the compartment is [Eq. (4)]:

$$t_{cd}(Na^+) + t_{cd}(Cl^-) + t_{cd}(OH^-) = 1 \tag{4}$$

The $t_{cd}(Cl^-)$ is a known value, as it has been experimentally determined. Then, assuming that at every moment concentration of Na^+ is equal to the initial value, the $t_{cd}(OH^-)$ can be calculated from the general equation for transference numbers [10] based on the electrical charge, mobility, and concentration of every specimen involved [Eq. (1)].

4.1.2. Zone II: anodic compartment

The chemical reactions assumed to take place in the anode are those corresponding to the corrosion of the electrode [Eqs. (5) and (5′)].

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{5}$$

$$Fe^{2+} \rightarrow Fe^{3+} + 1e^- \tag{5'}$$

Afterwards, it has been assumed that the cations of iron formed in the previous step suffer a process of hydrolysis [Eqs. (6) and (6′)]:

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 \downarrow + 2H^+ \tag{6}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 \downarrow + 3H^+ \tag{6'}$$

Considering that initially, the compartment was filled with deionized water, the species to be quantified are: chloride ions that come into the compartment through the specimen and H^+ ions generated from the electrodic reactions. Therefore, in the anolyte solution, Eq. (7) holds true.

$$t_{ad}(Cl^-) + t_{ad}(H^+) = 1 \tag{7}$$

As $t_{ad}(Cl^-)$ is known experimentally, $t_{ad}(H^+)$ can be directly calculated, which means that the amount of H^+ that migrates out of the compartment can be obtained.

4.1.3. Zone III: specimen

It has been assumed that in this zone, OH^- and H^+, coming from the catholyte and anolyte, respectively, will be neutralised stoichiometrically.

4.1.4. Determination of the experimental validation parameter (pH of the catholyte)

From an OH^- ionic balance in the catholyte compartment, it is observed that for each charge interval considered, "*i*," it can be stated that:

$$\begin{aligned}(OH^- \text{ catholyte})_i = &(OH^- \text{ catholyte})_{i-1} \\ &+ \text{generated } OH^- - \text{migrated } OH^- \\ &- \text{neutralised } OH^-)_i\end{aligned}$$

In this way, for each charge interval (between sampling), the OH^- concentration can be calculated, and from it, the corresponding pH that can be compared with that experimentally measured (Fig. 7). It is necessary to point out that estimated pH is calculated directly from OH^- concentration, while pH measured by a pH-meter takes into account the activity of the solution. This fact has been neglected in this research for the sake of simplicity, providing that a quite enough good accordance was noticed between measured and calculated pH, what confirms the suitability of the proposed phenomenological model and allows the pursuit of transference numbers of every species involved in the experiment.

4.2. Quantification of transference numbers in steady-state conditions

Fig. 8 illustrates an example that corresponds to the steady-state migration test with 0.2 M NaCl in the catholyte. This figure depicts the transference numbers for all the ionic species involved in the test in function of circulated charge: $t_{cd}(Cl^-)$, $t_{cd}(OH^-)$, $t_{cd}(Na^+)$, $t_{ad}(Cl^-)$ and $t_{ad}(H^+)$. Values corresponding to Cl^- are experimentally obtained; values corresponding to the rest of species are calculated according to the phenomenological model assumed.

This figure gives a complete picture of the behaviour of the system and allows to deduce the reasons for the three steps previously identified to represent migration of chloride to the anolyte as a function of time [9], and which can be explained in terms of the transference numbers of the species.

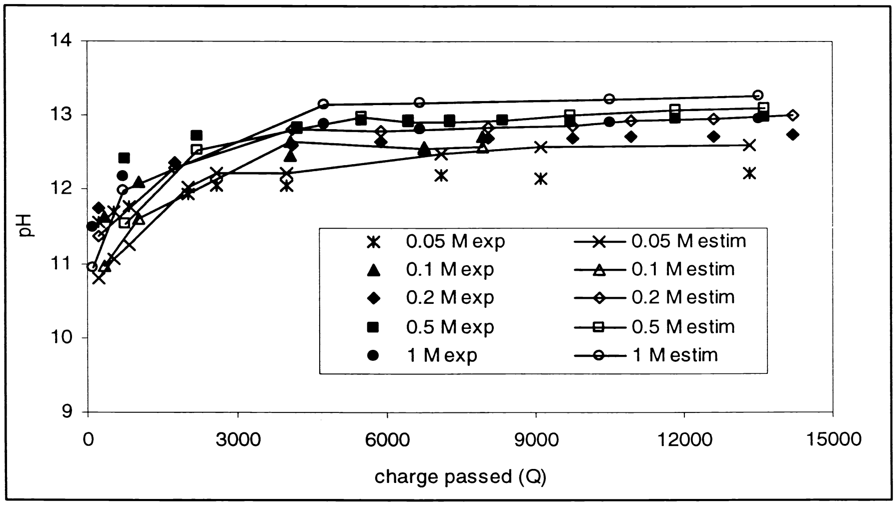

Fig. 7. Comparison between calculated (OH^-) and experimentally measured pH values of the catholyte.

Initially, in the catholyte, there are Cl^- and Na^+ ions that carry most of the current, being OH^- contribution negligible. However, in the anolyte, the maximum transference number corresponds to H^+ because the concentration of the rest of the ions is negligible. As the test proceeds, OH^- concentration increases in the catholyte as they are generated in the cathodic reaction; therefore, $t_{cd}(OH^-)$ increases while $t_{cd}(Cl^-)$ and $t_{cd}(Na^+)$ start to decrease gradually. On the other hand, chloride has started to arrive at the anolyte from the catholyte compartment (time lag is finished), and concentration of H^+ is not yet high (as not much charge has yet passed and H^+ is the ionic species having carried most of it in this compartment, which implies that most of them have migrated towards the catholyte); that is why a maximum in chloride anodic transference number is achieved. As a final step, a situation of practical stability in transference numbers is reached, because as $t_{cd}(OH^-)$ increases (due to its generation and to the decrease in chloride concentration), $t_{cd}(Cl^-)$ decreases and, consequently, the amount of chlorides that passes to anolyte decreases, too. As a consequence, there are H^+ ions, which again, in the anolyte, carry most of the current that circulates. Considering that $t_{cd}(OH^-)$ is lower than $t_{ad}(H^+)$, a considerable amount of the OH^- in the catholyte is neutralised by H^+ ions that arrive from the anolyte, which makes the system to almost reach an equilibrium.

4.3. Application to non-steady-state experiments

Providing that there is an unlimited source of chlorides in the catholyte, the application of the developed model indicates that the situation of stability in the transference number values should be also reached for the non-steady-state conditions (if an enough amount of charge had passed) before reaching the step of the steady-state period.

This has been experimentally validated from the series of non-steady-state migration tests, as can be seen in Fig. 9. This figure depicts the accumulative transference numbers $t_{cac}(Cl)$ for the different non steady-state tests in function of the electrical charge passed. Even in the conditions of the smaller amount of charge passed, the situation of stability of the $t_{cac}(Cl)$ seems to have been reached. As can be observed,

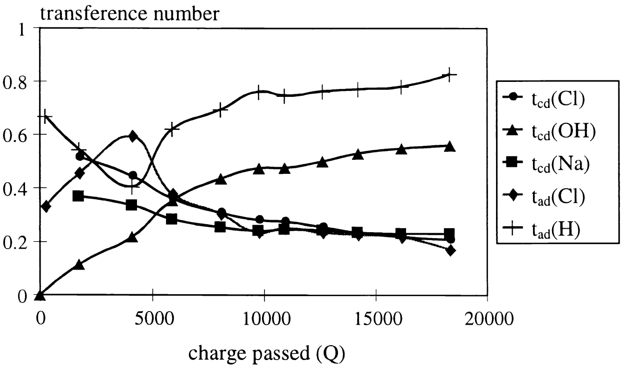

Fig. 8. Calculated evolution in the transference numbers of all ionic species involved in a steady-state migration test (initial concentration of NaCl in the catholyte = 0.2 M).

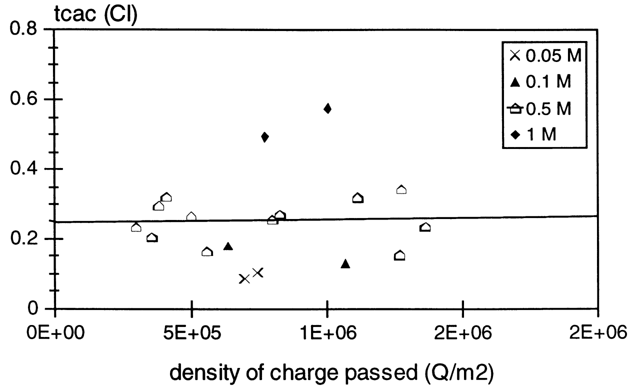

Fig. 9. Accumulative transference numbers $t_{cac}(Cl)$ for the different non-steady-state tests in function of the electrical charge passed.

for the concentration of 0.5 M, for which the amount of data is higher, the slope of the linear regression is equal to zero.

Therefore, it can be deduced that for each concentration tested, it is possible to obtain a characteristic $t_{\mathrm{cac}}(\mathrm{Cl})$, which represents the experiment in the equilibrium moment after a given amount of electrical charge has passed. For the series of experiments performed here, the minimum charge density is about 3.5×10^5 Q/m^2 (corresponding to 7 days, 0.5 M NaCl, and 150 mm depth). Therefore, from this value of charge, $t_{\mathrm{cac}}(\mathrm{Cl})$ stable values can be obtained.

The characteristic values for each concentration, found in present research, are presented in Table 3. It is necessary to point out that only the value corresponding to the concentration 0.5 M NaCl has been calculated with enough data to obtain a reliable average value. The values corresponding to the other concentrations in Table 3 are mainly given as a reference.

4.3.1. Simplified method

These deductions provide the basis of the development of a simplified method for the calculation of the non-steady-state diffusion coefficient of chlorides through concrete.

Provided that during the tests, charge densities higher than 3.5×10^5 Q/m^2 have circulated, $t_{\mathrm{cac}}(\mathrm{Cl})$ can be considered as a constant. Therefore, according to Faraday's Law, particularising for the chloride ions by means of the introduction of their transference number [2], the total amount of chlorides that have penetrated into the specimen, can be calculated according to the Eq. (8).

$$\frac{Qt_{\mathrm{cac}}(\mathrm{Cl})}{F} = \mathrm{Cl\ equivalents} \tag{8}$$

In Fig. 10, the comparison between the experimentally measured data and the calculated using Eq. (8), and the $t_{\mathrm{cac}}(\mathrm{Cl})$ values given in Table 3 can be seen. As can be seen, the accordance is very good.

Therefore, just from the registration of the current intensity during a non-steady-state migration test, it is possible to calculate the amount of chlorides that have penetrated into the specimen. If additionally, the surface concentration in the specimen, C_{s}, is analysed, from the integrated form of the second Fick's Law [Eq. (9)] [11], considering a semi-infinitum medium and external chloride concentration as a constant, the non-steady-state diffusion coefficient can be obtained by using, as a final step in the procedure, the analogy of treatment between migration and diffusion in non-steady-state conditions [12]. This analogy is based in the use of a "migration coefficient," D_{mig}, which enables to apply to a migration experiment any known solution of a diffusion problem [12], and is given by Eq. (10).

Table 3
Characteristic values of $t_{\mathrm{cac}}(\mathrm{Cl})$ for higher charge density passed than 3.5×10^5 Q/m^2

	$t_{\mathrm{cac}}(\mathrm{Cl})$			
	Number of data	Average	Standard deviation	Coefficient of variation
0.05 M	2	0.090	–	–
0.1 M	2	0.156	–	–
0.5 M	12	0.255	0.058	0.227
1 M	2	0.534	–	–

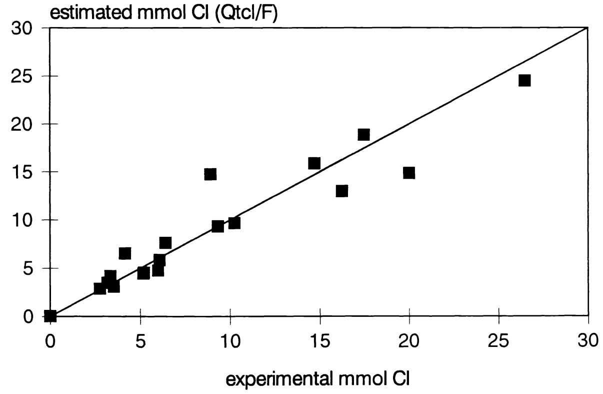

Fig. 10. Comparison between the amount of chlorides estimated and the experimentally measured.

Therefore, the final expression for the accumulative amount of chlorides in the specimen is given by Eq. (9):

$$M_t = 2C_{\mathrm{s}}\left(\frac{D_{\mathrm{mig}}t}{\pi}\right)^{\frac{1}{2}} \tag{9}$$

where M_t = amount of Cl$^-$ that have penetrated (mol/cm^2), C_{s} = surface concentration (mol/cm^3), and D_{mig} = migration coefficient.

Afterwards, it is necessary to calculate the corresponding non-steady-state diffusion coefficient from the accelerated D_{mig} in function of the characteristics of the tests, according to Eq. (10):

$$D_{\mathrm{mig}} = \frac{zF}{RT} D_{\mathrm{ns}} \frac{\Delta\phi}{2\ln l} \tag{10}$$

where $\Delta\phi$ = drop of voltage applied (V) and l = thickness of the specimen (cm).

4.3.2. A further simplification based on an assumed C_s

A further simplification would be possible if the measurement of the surface concentration, C_{s}, was avoided. From the obtained results, it can be deduced that, as well as the $t_{\mathrm{cac}}(\mathrm{Cl})$, from a given charge passed, the surface concentration is a constant for a given type of binder and external concentration (see Fig. 6b). Therefore, with the tabulation of the different C_{s} for different external chloride concentrations for OPC concretes of similar proportioning, and by the application of a factor different for each different binder, resulting from the different ability to bound chlorides (binding factor), the measurement of the chloride concentration would not be necessary in order to calculate D_{ns}. Just a simple migration test of the AASHTO type (ASTM C1202-91) would be enough. The authors are carrying out the determination of these binding factors in a statistical way.

5. Conclusions

Starting from the study of the steady-state migration tests, through the pursuit of transference numbers, a phenomenological model has been established and has been experimentally validated. This model allows the calculation of transference numbers of every species involved during the test. It has therefore enabled to identify and explain the reasons for the stages observed during a steady-state migration test.

The application of the phenomenological model to the non-stationary migration tests has allowed the development of a new simplified way to determine the non-steady-state diffusion coefficients, D_{ns}, just recording the current intensity circulating during the migration test, and the analysis of the surface concentration, C_s, after the test.

In addition, for avoiding the analysis of the C_s concentration, the possibility of tabulation of the different C_s for different external chloride concentrations in the same concrete types and the application of different "binding factors" for each kind of binder are posed. In this way, measurement of chloride concentration would be no longer necessary in order to calculate D_{ns}. Just a simple migration test of the AASHTO type (ASTM C1202-91) would be enough.

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