



Measurement of the steady and non-steady-state chloride diffusion coefficients in a migration test by means of monitoring the conductivity in the anolyte chamber Comparison with natural diffusion tests

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Abstract

The precise calculation of steady-state chloride diffusion coefficients is laborious, expensive, and time consuming due to the fact that it is necessary to take liquid samples for the chlorides to be analysed. In this paper, the concentration of chlorides is monitored by measuring the conductivity of the anolyte which initially is distilled water. Additionally, the calculation of D_s and D_{ns} is made from the same test using the concept of "time-lag" and of the "equivalent time" between diffusion and migration experiments. The correlation between D_s and the conductivity has been done by testing 10 different cementitious matrixes (concrete and mortar) with different binders, and considering the influence of the type of solution that is the source of chloride ions as well as the variation of the electrodes and the effect of the kind of matrix. The results obtained have been compared with natural diffusion results in order to validate them. As a result, for the possibility of making it automatic, the calculation of D_s and D_{ns} diffusion coefficients has been verified. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Diffusion; Migration; Chloride; Conductivity; Concrete

1. Introduction

The calculation of the time to steel reinforcement depassivation is becoming an urgent need due to the engineering demand of prediction of the service life of concrete structures. The initiation time of steel corrosion is composed of two steps: the time taken by the aggressive (chlorides in present case) to reach the reinforcement in a certain amount and the depassivation stage itself. Due to the uncertainties on the chloride threshold value, it is simply assumed to be a fixed value, and the majority of calculation methods of the initiation period are based in characterising the chloride diffusion coefficient, D .

However, it is often neglected the fact that at least two kind of coefficients can be obtained: one of them from

steady-state experiments using the so-called diffusion or migration cell [1–6], and the other from nonstationary experiments [7,8]. These coefficients are called in literature reversibly as effective, D_{eff} , or apparent, D_{app} , respectively. In order to avoid any confusion, in the present paper they will be named as D_s = stationary value of diffusion coefficient and D_{ns} = nonstationary value. D_s encounters only the ionic transport while D_{ns} also takes into account binding of chlorides with cement phases.

This difference concerning the consideration of chloride binding is very important when trying to use these values for prediction of the initiation period of rebar corrosion and when comparing different testing methods. Thus, any calculation of D_s from resistivity values (Modified Nernst–Einstein equation [3]) or from the Modified Nernst–Planck equation [3], leads to a value which cannot be directly used to predict service life or duration of the initiation period because it does not take into account chloride reaction. On the opposite, D_{ns} obtained from experiments that explicitly do take into account binding, might be used for predicting

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purposes, only provided that other factors such as concrete ageing or chloride external concentration had been taken into account.

To determine the D_s , the device used is the classical two compartments cell, where one of the chambers is filled with a chloride solution while the other contains a free chloride solution. Periodically along the experiment, Cl^- concentration in both compartments has to be monitored in order to determine the flux of chlorides throughout the specimen.

Two disadvantages are mainly attributed to this type of test: The first one is the fact that it is time consuming since getting the values of diffusion coefficients takes a very long time. On the other hand, since it is necessary to take liquid samples for the chlorides to be analysed, this kind of test is laborious as well as expensive.

The first disadvantage has been overcome by the application of an electrical field that accelerates the movement of chloride ions in the way that the time of testing can be shortened from several months to a few days. At present, this acceleration is being used by a greater number of authors [5–16]. However, the second inconvenience has not been solved yet.

In order to make this test less expensive and time consuming in steady-state conditions, in this paper, chloride concentration in the anolyte during a migration test has been correlated to the conductivity of the anodic solution.

Nevertheless, as has been mentioned before, in order to take chloride binding into account, it is necessary to calculate the D_{ns} . This calculation has been as well accomplished in present paper from the same test by means of calculating the time-lag taken by the chlorides to appear in the downstream or anolyte chamber. In this way, with a simple experiment, the two diffusion coefficients, D_s and D_{ns} , can be calculated without the need of making chloride analysis but through the simple monitoring of the conductivity of the anolyte. Several concrete and mortar mixes were tested.

2. Experimental

2.1. Materials

In order to cover in this study a wide range of conditions, several types of cementitious matrix with different kinds of binders have been used. Dosages of them are presented in Table 1. Eight different dosages of concretes, including several cements and additions of fly ash (FA) and silica fume (SF) have been used in the study, as well as two mortar compositions.

All the specimens were cylindrical of 75 mm in diameter and 150 mm in high. They were demoulded after 24 h of being cast and cured during 28 days under water or in a humid chamber (>95% HR). Slices of 10 mm thick were cut from the centre of the specimen in order to avoid heterogeneity and then just before the migration test, they were water-saturated under vacuum following the standard ASTM C1202-91.

2.2. Procedures

Two kinds of chloride penetration regimes have been carried out: In steady-state (migration and diffusion tests), and in non-steady-state (only natural diffusion tests) conditions.

2.2.1. Steady-state tests

2.2.1.1. Migration tests. To perform the steady-state migration tests, a two-compartment cell [3], as shown schematically in Fig. 1, was used.

Parameters taken into account for this study have been:

(a) Influence of type of solution, which is the source of chloride ions, as well as the type of electrodes: by means of two series of tests with the same type of concrete (Dosage 1). For one of the series, steel electrodes and NaCl in the catholyte were used. In the other, electrodes of

Table 1
Dosage of the materials used

	Dosage									
	1	2	3	4	5	6	7	8	9	10
Type of matrix	C	C	C	C	C	C	C	C	M	M
Cement	OPC	I-42.5 R/SR	I-42.5 R/SR	I-42.5 R/SR	I-42.5 R/SR	II-AV/ 42.5 R	IV-B/32.5 SR/BC	I-52.5 R	IV-B/32.5 SR/BC	IV-B/32.5 SR/BC
Addition	–	–	FA 140	SF 36	–	–	–	–	–	–
W/C	0.4	0.45	0.45	0.45	0.4	0.4	0.4	0.4	0.37	0.49
Cement (kg/m ³)	380	400	260	364	400	400	400	400	708.3	–
Cement + sand	–	–	–	–	–	–	–	–	–	1948
Sand (kg/m ³)	771	911	911	911	925	925	925	925	1239.4	–
Gravel (kg/m ³)	1177	949	949	949	885	885	885	885	–	–
Superplasticizer	no	yes	yes	yes	yes	yes	yes	yes	yes	yes

C = concrete; M = mortar.

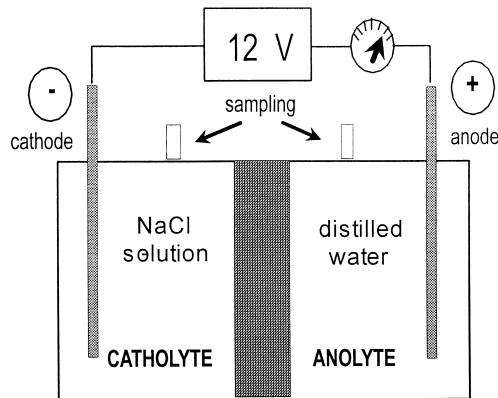


Fig. 1. Experimental arrangement used in migration tests.

Cu and CuCl_2 as source of chloride ions were employed. For each one of these series, five different concentrations of chloride ion in the catholyte were tested (0.05, 0.1, 0.2, 0.5, and 1 M).

(b) Influence of the type of concrete: Working with the same kind of electrodes (steel) and the same solution as source of chlorides in the catholyte (1 M NaCl), tests with Dosages 1–10 of Table 1 were carried out.

Distilled water was introduced in the compartment where the anode was located (anolyte) in all the cases. This neutral solution avoids chlorine evolution in the anode by inducing its own corrosion. The voltage applied was of 12 V DC, although the real voltage drop across the specimen was measured as indicated in Ref. [3]. Periodically along the experiment, samples in both compartments were taken and concentration of chlorides was analysed by potentiometric titration. Just after taking the samples, the electrical field was switched off and after waiting for 5 s, conductivity of the anodic solution was measured by introducing an electrode of conductivity in the compartment. Values of conductivity were referenced to a tem-

perature of 25°C, by considering an increase of 2% in the conductivity of the solution when temperature increases a degree centigrade.

Once the conductivity was recorded, the electrical field was switched on again to continue the test.

2.2.1.2. Natural diffusion tests. In addition, validation of the diffusion coefficients obtained by migration tests has been carried out. This has been done by comparison with those obtained by steady-state natural diffusion tests by a series of tests using the dosage of Concrete 1 at different concentrations of NaCl in the compartment source of chloride ions (0.05, 0.1, 0.5, and 1 M). The series with CuCl_2 as source of chloride ions was not performed in this case.

For these tests, procedure and devices used were the same as for migration tests but without application of the electrical field. The holes in the cell (Fig. 1) designed to introduce the electrodes were sealed with rubber taps in order to avoid the evaporation of the solutions.

2.2.2. Natural diffusion in non-steady-state tests

In order to compare the non-steady-state diffusion coefficients, D_{ns} , obtained from the “time-lag” in the steady-state migration tests (described in following paragraphs) with those of natural diffusion, a series of natural diffusion tests in non-steady-state were carried out on the specimens of dosage labelled as 1. To perform these tests, an arrangement of “ponding” type was used [8], made by sealing a tank on the top of the specimen where the solution of chlorides is stored. The testing period was of 15 months, and external solutions of NaCl 0.05, 0.1, 0.5, and 1 M were used.

At the end of each experiment, the specimen was grinded in steps of 2 mm each. These samples were analysed by X-ray fluorescence in order to obtain the concentration of chlorides (percentage of Cl^- by weight of sample).

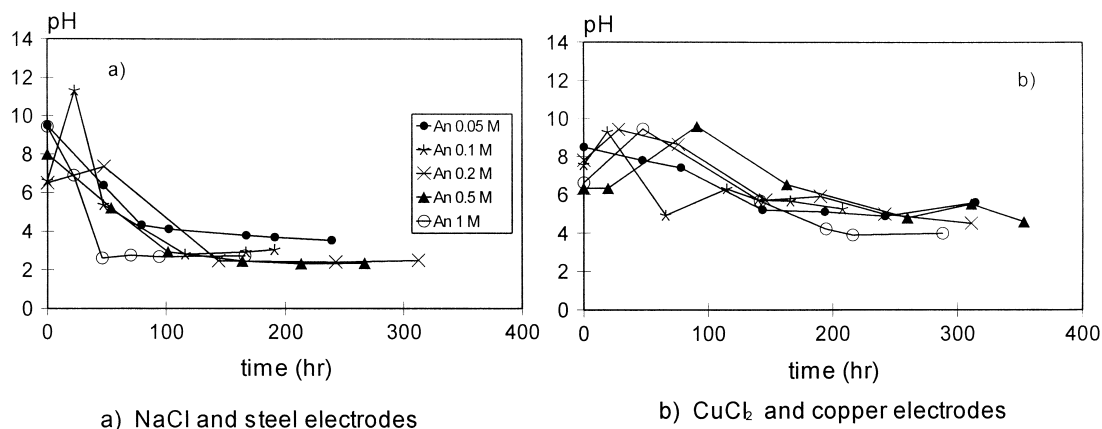


Fig. 2. (a,b) Evolution of pH in the anolyte for the two series of different chloride concentrations for concrete “Dosage 1.”

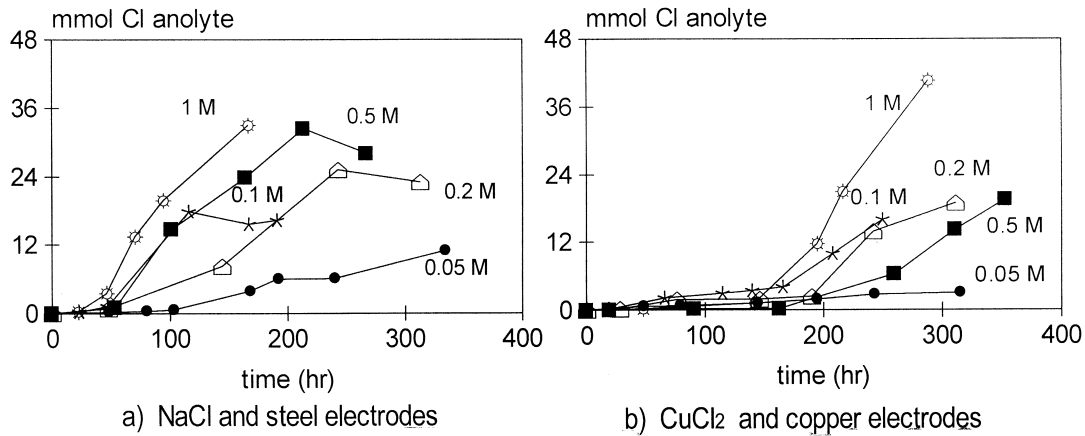


Fig. 3. (a,b) Evolution in the amount of Cl^- in anolyte chambers for the two sets of experiments with steel and copper electrodes and different Cl^- concentrations as initial testing solutions.

2.3. Calculation of the diffusion coefficients

2.3.1. Natural diffusion tests

2.3.1.1. Steady-state. From natural diffusion tests, chloride diffusion coefficients were calculated according to the first Fick's law (Eq. (1)) [17]:

$$\ln(C(U)_1\gamma - C(D)) = -\frac{D_s A}{Vl}(\Delta t) + \ln(C(U)\gamma) \quad (1)$$

where: $C(U) = \text{Cl}^-$ concentration in the source compartment (upstream compartment) (mol/cm^3); γ = activity coefficient of the solution in the source compartment; $C(D) = \text{Cl}^-$ concentration in initially chloride free compartment (downstream compartment) (mol/cm^3); D_s = effective (steady-state) diffusion coefficient (cm^2/s); V = volume of the downstream compartment (cm^3); Δt = diffusion time (s); A = diffusion area (cm^2); l = Thickness of the specimen (cm).

2.3.1.2. Non-steady-state. Calculation of D_{ns} from natural diffusion tests were done by fitting the chloride profiles to the second Fick's Law equation for a semi-infinite media (Eq. (2)) [17]:

$$C(x, t) = C_s \left(1 - \text{erf} \frac{x}{2\sqrt{D_{nst}}} \right) \quad (2)$$

where: D_{ns} = apparent diffusion coefficient (cm^2/s); C_s = surface concentration of chlorides; $C(x, t) = \text{Cl}^-$ concentration at any distance, x , at any time t .

2.3.2. Migration tests

2.3.2.1. Effective (steady-state) diffusion coefficient, D_s . Calculation of the diffusion coefficients, from migration tests, was made using the Modified Nernst–Planck equation (Eq. (3)) [3].

$$D_s = \frac{J_{\text{Cl}} RTl}{zFC_1 \gamma \Delta \Phi} \quad (3)$$

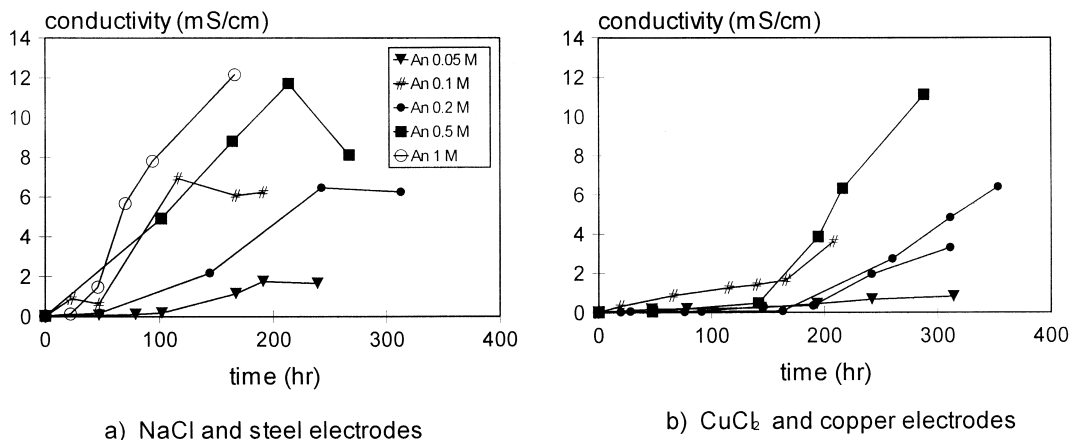


Fig. 4. (a,b) Evolution of the conductivity values (mS/cm) at 25°C in the anolyte chambers for the two sets of experiments with steel and copper electrodes and different Cl^- concentrations as initial solutions.

where: J_{Cl} = flux of chlorides ($\text{mol}/\text{cm}^2 \text{ s}$); $C_1 = \text{Cl}^-$ concentration in the catholyte (mol/cm^3); γ = activity coefficient of the catholyte solution; $\Delta\Phi$ = effective voltage applied (V); l = thickness of the sample (cm).

2.3.2.2. Apparent diffusion coefficient, D_{ns} . The calculation of the apparent diffusion coefficient, D_{ns} , has been done in the following way: From Ref. [18], the enhancement ratio when applying an electrical field, or the time that chlorides would have taken during a natural diffusion test to reach the same depth than during a migration test can be calculated (Eq. (4)):

$$\frac{t}{t_{\text{dif}}} = \frac{6}{v^2} \left[v \coth \frac{v}{2} - 2 \right] \quad (4)$$

where: t = time-lag in the migration test; t_{dif} = time equivalent to t if no electrical field would have been applied (s); $v = ze\Delta\phi/kT$; k = Boltzmann's constant.

This mathematical solution allows to “convert” migration tests into natural tests. That is to say, using this “equivalent” time, t_{dif} , D_{ns} is directly obtained (Eq. (5)) [17] from:

$$D_{ns} = \frac{x_d^2}{6t_{\text{dif}}} \quad (5)$$

where: x_d = thickness of the specimen (cm).

3. Results

3.1. Steady-state tests

3.1.1. Migration tests

3.1.1.1. Influence of type of solution source of chloride ions and type of electrodes. For these experiments, the concrete of Dosage 1 (see Table 1) was submitted to two series of tests: The first one with steel electrodes and NaCl in the

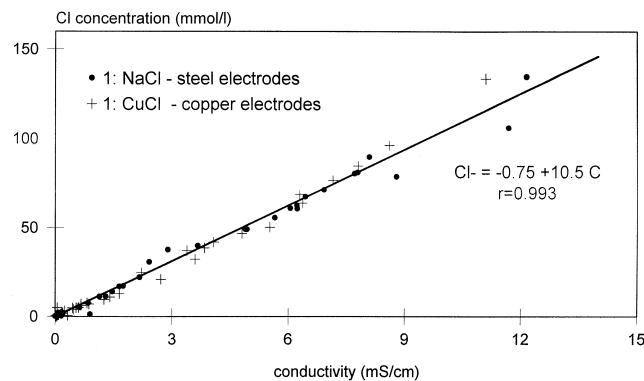


Fig. 5. Conductivity values (25°C) vs. the corresponding chloride concentration (anolyte compartment) having initially distilled water, for different Cl^- concentrations (0.05, 0.1, 0.5, and 1 M) in the catholyte, for the two series tested (steel electrodes and NaCl and electrodes of Cu and CuCl_2 as source of chloride ions).

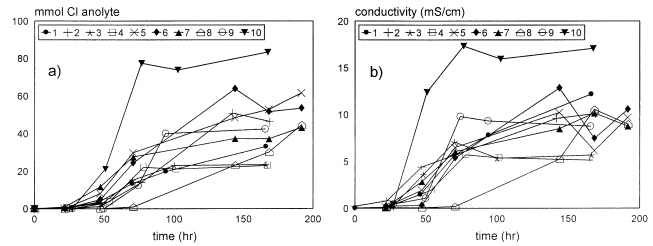


Fig. 6. (a,b) Evolution in the (a) amount of Cl^- , and (b) conductivity in anolyte chambers for the 10 different dosages. Steel electrodes and 1 M NaCl in the catholyte.

catholyte, and the other with electrodes of Cu and CuCl_2 as source of chloride ions.

It is necessary to point out that as the electrodes used in the two series are different, the electrodic reactions are consequently different, leading to different final anolyte solutions, as can be seen in Fig. 2(a,b).

Fig. 3(a,b) shows the evolution of the amount of chloride ions in the anolyte chamber for the two series of experiments.

It can be observed that the amount of chlorides in the anolyte chamber increases along time according to the known trend: initially, there is a period in which the amount of chlorides that passes to the anolyte is negligible. Its duration corresponds to the so-called “time-lag,” and can be defined as the necessary time for chlorides to pass through the concrete disc, saturating it. This period of time will be used later in order to obtain the D_{ns} values. After this period, the flux of chloride ions through the specimen is constant and corresponds to a steady-state period.

In Fig. 3, it can be noticed that time-lags corresponding to the series with electrodes of Cu and CuCl_2 , are longer than those corresponding to the NaCl and steel electrodes, which was attributed to the differences in binding of chlorides by the solid phases. Thus, with steel electrodes and NaCl solution, the amount of bound chlorides is smaller than when Cu/ CuCl_2 is used. The justification of this behaviour is given in Ref. [19] and is out of the scope of present paper.

Fig. 4(a,b) depicts the values of conductivity measured in the anolyte at different times of the experiments. Comparing the values of conductivity with those of the amount of chloride ions in the anodic compartments (Fig. 3), it can be realised that there is a close relationship between these two parameters. This can be seen in Fig. 5, where, for the two series, conductivity values have been plotted vs. the corresponding chloride concentration in the anolyte. There is a clear linear relationship with a regression coefficient of .993.

3.1.1.2. Influence of the type of matrix. A series of steady-state migration experiments using the same kind of electrodes (steel) and the same solution as source of chlorides in

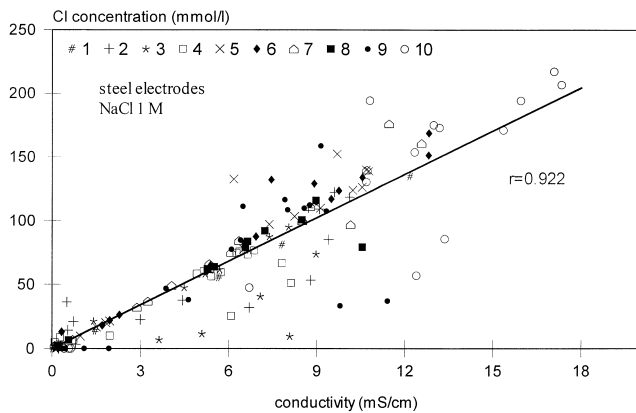


Fig. 7. Conductivity values (25°C) vs. the corresponding chloride concentration (anolyte compartments) for samples corresponding to 10 different dosages.

the catholyte (1 M NaCl) but for 10 different dosages (1 to 10 in Table 1) was also carried out.

Fig. 6(a,b) shows the evolution of the amount of chlorides in the anolyte chamber for the 10 different dosages, as well as the values of conductivity recorded in the anolyte compartments along the time for these experiments.

In the same way that it was done for the series with different experimental conditions, in Fig. 7, the conductivity values corresponding to the different dosages have been plotted vs. the chloride concentration. It can be seen in Fig. 7 that the scatter among the data is higher than in the previous case (Fig. 5). However, a linear relationship has been found, with a regression coefficient of .922. This scatter has not been attributed to any particularity of the different dosages tested, and therefore it has been considered as randomly distributed.

3.1.2. Diffusion tests

The results obtained with the series of natural diffusion tests (for Dosage 1), in order to be compared with the

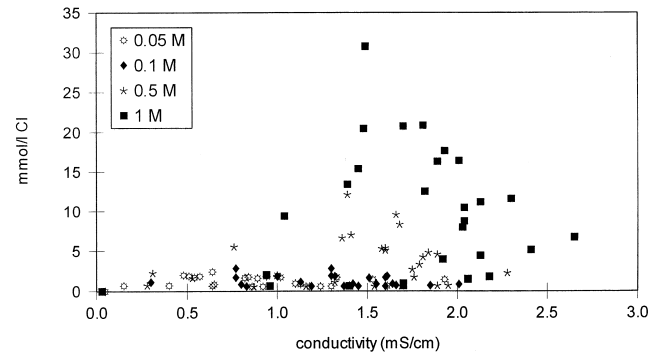


Fig. 9. Chloride concentration in function of the conductivity values (25°C) for the downstream compartment in natural diffusion tests.

migration tests, are presented in Figs. 8 and 9. Fig. 8(a) shows the evolution of the amount of chlorides that has passed to the downstream compartment, and Fig. 8(b) shows the evolution of the values of conductivity in function of the testing time.

However, as can be noticed in Fig. 9, a relationship between chloride concentration and conductivity in the downstream compartment cannot be found for the natural diffusion tests.

Therefore, this procedure of determining the concentration of chlorides in the downstream compartment by means of measuring the conductivity seems not to be valid for natural diffusion tests. This fact is attributed to the leaching of ions (mainly OH^-) from the specimen due to the longer duration of the tests, an effect that masks the variation of the conductivity due to the chloride ions alone.

3.2. Non-steady-state tests

Fig. 10 shows the chloride profiles obtained after the tests for the different concentrations tested with Dosage 1 (percentage with respect to dry sample).

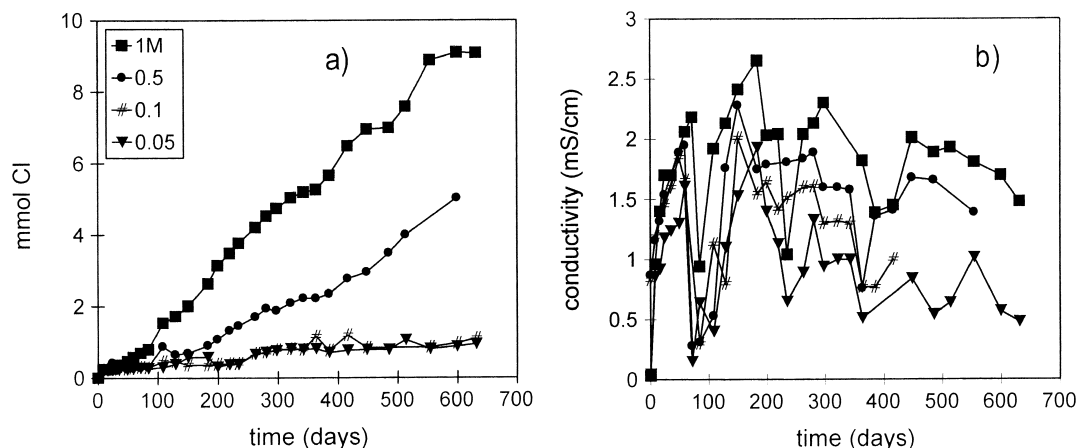


Fig. 8. (a,b) Evolution in the amount of chlorides (a) and conductivity at 25°C (b) in the downstream compartments for the natural diffusion experiments.

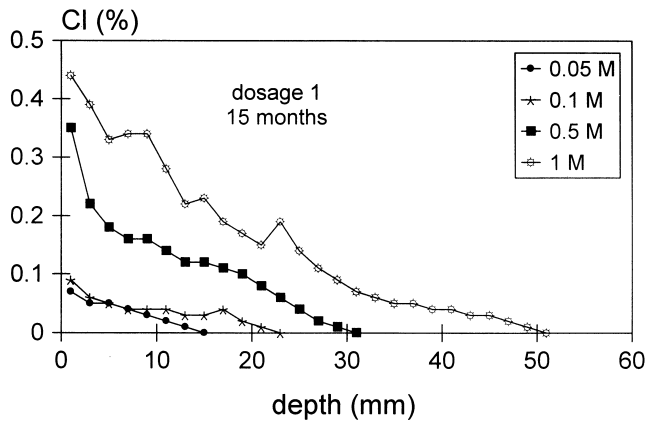


Fig. 10. Chloride profiles obtained at the end of each experiment for Dosage 1 of concrete.

3.3. Calculation of the diffusion coefficients

3.3.1. Steady-state diffusion coefficients

The comparison between the diffusion coefficients obtained by diffusion and migration tests, has been done for the dosage of concrete labelled as 1 (Table 1). The D_s calculated from the flux of chlorides passing to the downstream compartment are given in Table 2, for the natural diffusion and migration (Eqs. (1) and (3), respectively).

It can be noticed that the diffusion coefficient obtained from migration tests for the concentration of chlorides of 0.05 M does not follow the decreasing trend of the rest of the concentrations tested, typical of variation of the D_s with concentration. This has been attributed to the fact that at so low concentrations of chlorides, the concentration in the catholyte cannot be considered as constant [20], and therefore, the hypotheses on which the calculations are based, are not fulfilled. In the case of using so low concentrations, an infinite source of chlorides has to be used to have reliable results [20].

3.3.2. Non-steady-state diffusion coefficients

The D_{ns} calculated from the profiles of Fig. 10 and using Eq. (2), as well as the values calculated from the migration tests according to the Eqs. (4) and (5), are given in Table 3. It can be easily that the values differ, which will be commented later.

Table 2
Obtained by migration and diffusion tests

$[Cl^-]$ (M)	Diffusion (cm^2/s)	Migration (cm^2/s)
0.05	1.043E-8	2.70E-8
0.1	0.976E-8	6.26E-8
0.2	—	2.02E-8
0.5	0.889E-8	1.24E-8
1	0.887E-8	0.74E-8

4. Discussion

4.1. Conductivity measurements to determine the chloride concentration in the downstream compartment in migration and diffusion tests

The determination of the chloride flux implies taking samples of the anolyte solution and analysing them to determine the chloride content, in order to graphically represent the accumulated amount of chlorides in function of the duration of the test. This process makes the experiments hard to perform (as it is necessary to take samples every few hours in order not to lose the steady-state period), as well as expensive, as chlorides analysis are not cheap. This is the reason of the importance of the development of a way to calculate the D_s , but avoiding the, until now, inherent sampling.

In this respect, the results found in present experimentation have shown the following.

(1) For migration experiments, using distilled water as the initial anolyte solution, for the same concrete, irrespective of the experimental conditions, chloride concentration in the anolyte can be obtained from a simple measurement of the conductivity of the solution. The very good correlation obtained for the series using Dosage 1 (see Fig. 3), makes it clear that from the measurement of the conductivity in the anolyte, it is possible to obtain directly the amount of chlorides in the anodic solution, independently of the kind of the electrodes and of the nature and initial concentration of the cathodic source solution. It is important to point out that the initial solution in the anolyte has to be distilled water, because its low initial conductivity allows the easy detection of chlorides as soon as they start to pass to the anolyte [21]. When using another initial solution, the increase in conductivity can be masked due to the presence of other ions. This effect was reported in Ref. [22], where starting with a solution of NaOH + KOH in the anolyte, a progressive decrease in the values of the conductivity in the anolyte was detected.

This masking effect has been detected when trying to determine the chloride concentration in the downstream compartment in a natural diffusion test. In this case, the masking ions are those coming from the own specimen due to the long duration of the tests. This method of measuring the conductivity in the downstream compartment seems therefore, not to be valid for natural diffusion tests.

Table 3
 D_{ns} obtained by migration and diffusion tests

$[Cl^-]$ (M)	From time-lag (migration) (cm^2/s) (Eqs. (4) and (5))	From diffusion (cm^2/s) (Eq. (2))
0.05	1.73E-8	1.6E-8
0.1	2.23E-8	3.20E-8
0.2	1.46E-8	—
0.5	2.28E-8	3.96E-8
1	2.76E-8	5.12E-8

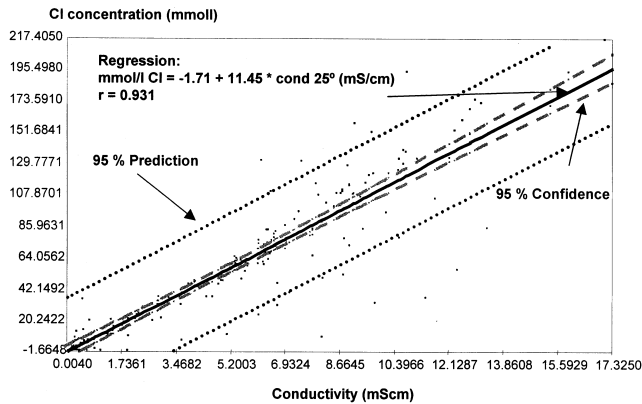


Fig. 11. Concentration of chlorides in the anolyte in function of the conductivity of the solution including the data from all the experiments and the confidence analysis.

(2) For different dosages, with the same type of electrodes and catholyte solution, any differences coming from the different type of binder have not been noticed, as the correlation coefficient is quite good provided that 10 different types of dosages, including concretes and mortars, are depicted together (see Fig. 7).

Therefore, the last step consists in finding a unique correlation among concentration of chlorides in the anolyte and conductivity. Thus, all the series of experiments (data in Figs. 5 and 7) have been plotted together. The results can be seen in Fig. 11.

In Fig. 11, the confidence analysis on the data can be seen: the range of 95% of confidence and those of 95% of prediction.

The correlation coefficient found is rather good: $r = 0.931$, resulting in the final equation (Eq. (6)):

$$[\text{Cl}^-] (\text{mmol/l}) = a_0 + a_1 \times x$$

$$= -1.71 + 11.45$$

$$\times \text{Conductivity } (25^\circ\text{C}) (\text{mS/cm}). \quad (6)$$

The standard error for $a_0 = 1.900$; the standard error for $a_1 = 0.301$, and the residual standard deviation is 19.193.

Provided that the value of the residual deviation are mainly due to a few points, that we are dealing with concrete experiments, and the errors and bias associated to every laboratory analysis, this correlation can be considered good enough for prediction purposes. Therefore, it is possible to calculate the chloride concentration in the anolyte automatically by introducing a conductivity electrode, connected to a data logger, into the anodic compartment of a migration cell. In this way, the device should be programmed to take data every settled amount of time until decrease or no more noticeable increase in the conductivity are detected, which would mean the end of the test.

4.2. Determination of the chloride diffusion coefficients from migration tests

4.2.1. Steady-state, D_s

From Tables 2 and 3, it can be deduced that the agreement between the diffusion coefficients obtained from migration and diffusion tests is not found for all chloride concentrations, for both D_s and D_{ns} .

In the case of D_s , the accordance is very good for 1 M and fairly good for 0.5 M. The disagreement for the lowest concentrations can be attributed to several reasons: on one hand, the differences in the amount of chloride binding between migration and diffusion tests, as was explained in another paper [23], where chloride binding isotherms were calculated and discussed. At lower concentrations, the amount of chlorides bound in a migration test is smaller than expected. However, at higher concentrations, combined chlorides are similar for migration and natural diffusion tests [23]. On the other hand, another reason might be that below a determined concentration of Cl^- in the catholyte compartment, the amount of chlorides is depleted during the experiment in such a way that the current is mainly carried out by other species that are present in the electrolytes [20]. Therefore, below a concentration of 0.2 M in NaCl (when using conventional cells), the amount of chlorides is not enough to provide an optimum efficiency in the transport of the current by the chlorides, as it was justified in Ref. [20].

Therefore, migration tests should be performed with chloride concentration in the catholyte higher than 0.5 M NaCl, in order to have results comparable to those of natural diffusion.

4.2.2. Non-steady-state, D_{ns}

Regarding the results of D_{ns} , it is necessary to point out that different experimental conditions in non-steady-state lead to different diffusion coefficients obtained even when only natural diffusion is involved [24]. The reason is that D_{ns} coefficients are variable not only in function of the external concentration, but also with the duration of the test.

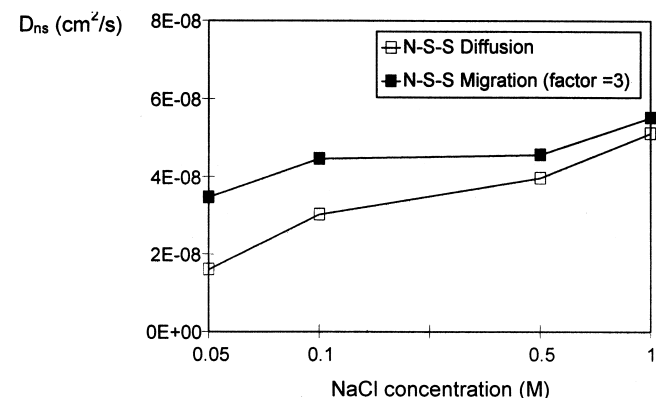


Fig. 12. Final comparison between chloride diffusion coefficients from diffusion and migration tests in non-steady-state conditions.

When migration experiments are used, additional complexity is introduced.

Comparing the values obtained (Table 3), those from migration tests are found to be lower than those corresponding to natural diffusion tests. This lack of agreement has been attributed to the multiplying factor used in the denominator of the time-lag equation (Eq. (5)). If instead of using a factor of 6 in Eq. (5), a factor of 3 is applied, the results obtained are coherent with the previously discussed binding phenomena and in good accordance with those of natural diffusion, as can be seen in Fig. 12.

It is known that the multiplying factor in the denominator of the time-lag equation appears after the integration of the differential equation. It also appears in the phenomenological treatment of the ionic “random walk” as a result of the movement of the ions in three dimensions. Finding that the best fitting factor is 3 instead of 6 could be interpreted as due to the fact that the electrical field restricts the random walk because it directs the movement of the ions depending of their polarity. However, this is simply a hypothesis that should be better verified.

4.3. Proposed methodology

According to the results obtained, the methodology proposed to calculate simultaneously the steady, D_s , and non-steady, D_{ns} , diffusion coefficients in a nonlaborious way is given below.

A unique test has to be carried out: a steady-state migration test in a two-compartment cell. The anodic solution must be distilled water and the cathodic one NaCl 1 M. The voltage drop between steel electrodes should be around 12 V DC.

A conductivity electrode, connected to a data logger, has to be introduced into the anodic compartment of the migration cell. The chloride concentration in the anolyte is then

calculated by means of Eq. (6). The final calculation of the D_s will be done by application of the Modified Nernst–Planck equation (Eq. (3)).

Regarding the D_{ns} , it will be calculated from the time-lag obtained by the intersection of the straight line of chloride flux characteristic of the steady-state with the x -axis (Fig. 13), and later application of Eqs. (4) and (7), as explained previously.

$$D_{ns} = \frac{x_d^2}{3t_{dif}} \quad (7)$$

5. Conclusions

The conclusions derived from present work can be summarised as follows.

(1) Chloride diffusion coefficients through concrete (D_s and D_{ns}) can be obtained from steady-state migration experiments, taking into account that the chloride concentration in the catholyte must be higher than 0.5 M NaCl (1 M is recommended), in order to have results comparable to those of natural diffusion experiments. Among other reasons, concentrations below 0.5 M promote lower chloride binding in migration tests than in natural diffusion ones.

(2) A good relationship between the value of chloride concentration and conductivity in the anodic compartment of a migration test in steady-state has been obtained. This correlation can be used independently of the type of electrodes, binder and cementitious matrix. In addition, it is also independent of the nature and initial concentration of the cathodic source solution. That is to say, for every experimental condition chosen, provided that the initial solution in the anolyte is distilled water, it is possible to calculate the flux of chlorides through the specimen by applying the equation:

$$[Cl^-] \text{ (mmol/l)} = -1.71 + 11.45$$

$$\times \text{Conductivity (25}^\circ\text{C) (mS/cm)}.$$

(3) In consequence, important advances from a practical point of view can be derived. Thus, it is possible to automate the calculation of the diffusion coefficient in steady-state conditions, D_s , by introducing a conductivity electrode into the anodic compartment, connected to a data logger, in the way that sampling and analysing chlorides during the tests can be avoided.

(4) From the same test, the non-steady-state diffusion coefficient, D_{ns} , can be calculated from the value of time-lag obtained during the migration test and application of Eqs. (4) and (7) based in the concept of equivalent time between diffusion and migration.

(5) The procedure of measuring the conductivity for monitoring chloride diffusion is not valid for natural diffusion tests because the effect of leaching of ions from the

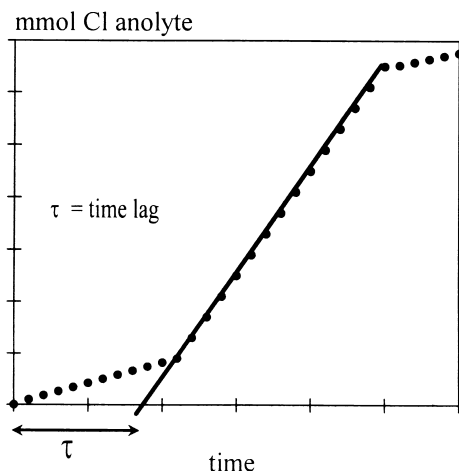


Fig. 13. Determination of the value of time-lag from a migration test.

concrete specimen disguises the increase in the conductivity due to the chloride ions.

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