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A new way for determining the chloride diffusion coefficient in concrete from steady state migration test

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Abstract

This paper presents a new method for measuring the chloride diffusion coefficient in concrete from steady state migration tests. First, we review concepts of the steady-state diffusion and migration tests. We emphasize that these tests have limitations if we use them in the classical way. Then, we show how it is possible to determine the chloride diffusion coefficient from a steady-state migration test by measuring the drop in chloride concentration in the cathodic solution. Four different concretes were tested to show the influence of the cement and the water/cement ratio. The results are as accurate as those obtained with an ordinary method. Moreover, it is easy to make use of this method and the length of the test is now comparable with the time spent in using a non-steady state experiment. A numerical model based on a finite difference method allows us to illustrate some equations.

Keywords: Diffusion; Transport properties; Chloride; Modeling

1. Introduction

To predict the service life of concrete in marine environments, we have to know the flow rate of chloride ions through a unit area of concrete. Therefore, we have to know both the effective chloride diffusion coefficient D_e and the chloride binding isotherms. Thereafter, experimental evaluations of the effective chloride diffusion coefficient in particular are discussed. We have two different approaches to determine the effective chloride diffusion coefficient. A numerical model based on a finite difference method [1] allows us to illustrate some equations. First, we can use a pure steady state diffusion test [2]. During the experiment, the measurement of the chloride concentration in the downstream cell allows us to calculate the diffusion coefficient once the steady state is reached by using Fick's law. By referring to Fig. 1 we can observe the increase of chloride concentration in the downstream cell that is simulated by using a numerical model. Two curves are presented to show the chloride binding effect on the same concrete. It must be emphasized that this chloride binding was assumed to be instantaneous in the simulations.

We can see that this binding effect does not modify the determination of the diffusion coefficient since it has no influence on chloride ion flux in the steady state. Chloride binding just leads to an increase in time lag [2]. Therefore, this method seems to be an efficient way to find the diffusion coefficient. However, steady state diffusion tests have an important drawback. Indeed, the experiments are time-consuming and we can't use this kind of test as a standard procedure.

Since diffusion experiments are time-consuming, steady state migration tests were developed to accelerate chloride ions through the concrete [3–7]. This is the second possibility that we have to measure the effective chloride diffusion coefficient in concrete. As in the previous case, the flux of chlorides is measured in the downstream cell at the anode (cf. Fig. 2).

As the flux becomes constant, Nernst-Planck's relation [3] allows us to deduce the value of the diffusion coefficient, as seen in Eq. (1):

$$-J(x) = D_e\frac{\partial c}{\partial x} + \frac{zF}{RT}D_e c\frac{\partial U}{\partial x} + cv(x) \quad (1)$$

It must be noticed that in this equation, the concentration is assumed to be equal to the activity of chlorides. Indeed, according to Arsenault [8], the influence of the activity coefficient on the flux of chlorides is negligible. In Eq. (1),

J(x): flux (mol/m^2/s)
c: concentration (mol/m^3)
D_e: diffusion coefficient (m^2/s)
z: valence number

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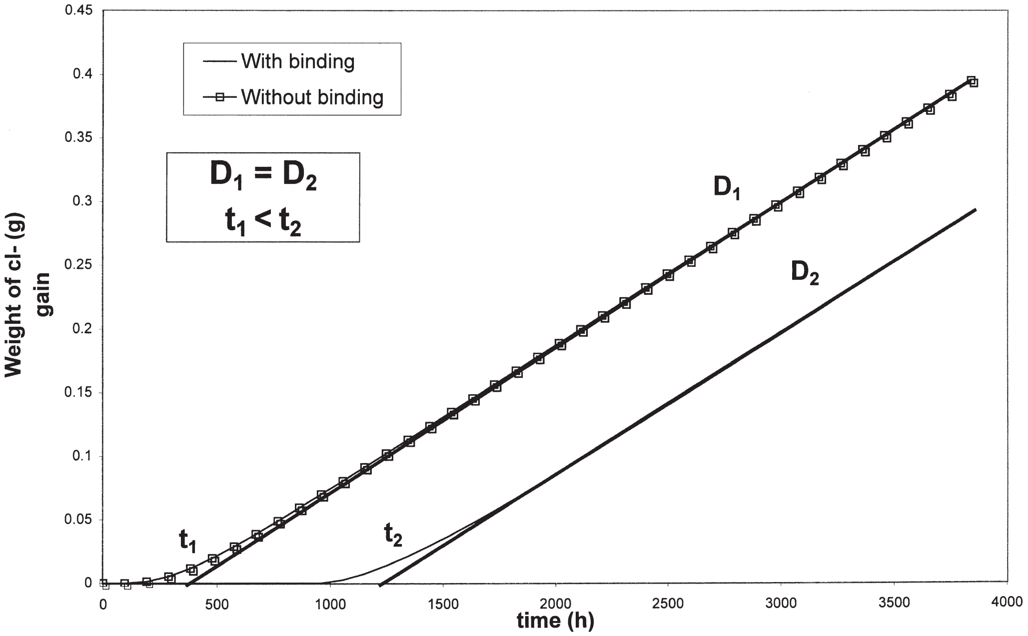

Fig. 1. Diffusion test simulation ($D_e = 2.10^{-12}$ m^2/s, thickness = 1 cm, $c_{up} = 0.564$ mol/L upstream).

F: Faraday's constant [J/(V • mol)]
U: potential (V)
R: gas constant [J/(mol • K)]
T: temperature (K)
$v(x)$: velocity of solute (m/s)

Since the concrete is saturated, the velocity of solute can be neglected. By assuming a constant electrical field across the sample, Eq. (1) can be simplified [3] and then we obtain [see Eq. (2)]:

$$D_{e,\text{down}} = \frac{1}{c_{\text{up}}}\frac{RT}{F}\frac{J_{\text{down}}}{E} \quad (2)$$

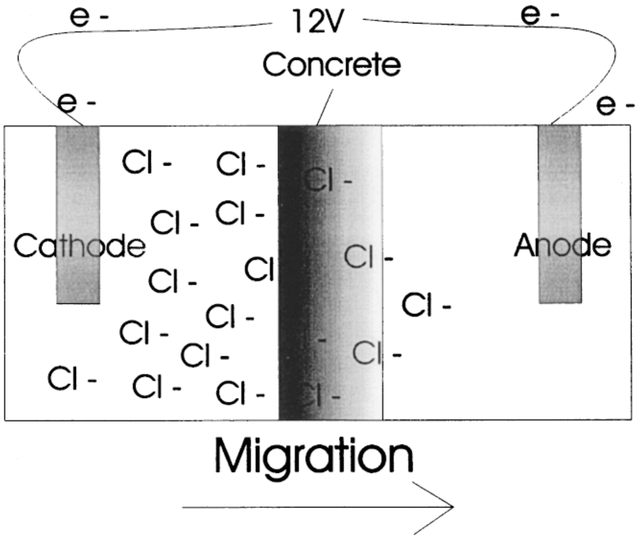

Fig. 2. Migration experiment principle.

where

E: electrical field (V/m)
J_{down}: ion flux in the downstream cell in steady state (mol/m^2/s)

From Nernst-Planck's relation and a numerical model based on a finite difference method (cf. Fig. 3) we can, as in the diffusion case, verify that chloride binding has an influence upon time lag but it does not alter the value of the diffusion coefficient.

Therefore, we are able to determine the diffusion coefficient of concrete within a short period by using the migration test. However, it is important to notice that the calculation of the diffusion coefficient from the measurements of the chloride ion concentration in the downstream cell is based on many assumptions:

To establish a steady state, the concentration gradient must be constant during the test. Therefore we have to renew the upstream and downstream solutions frequently.

Chloride ions interact with concrete and this leads to a decrease of the chloride ion penetration rate within the concrete sample. We have seen previously that this phenomenon does not affect the value for the effective diffusion coefficient, but it increases the time lag. The tests must last longer so that the diffusion coefficient can be determined with good accuracy.

To obtain an accurate value for the diffusion coefficient, it is necessary to measure carefully the amount of chloride ions that get into the concrete sample. However, during a migration test, chemical reactions may

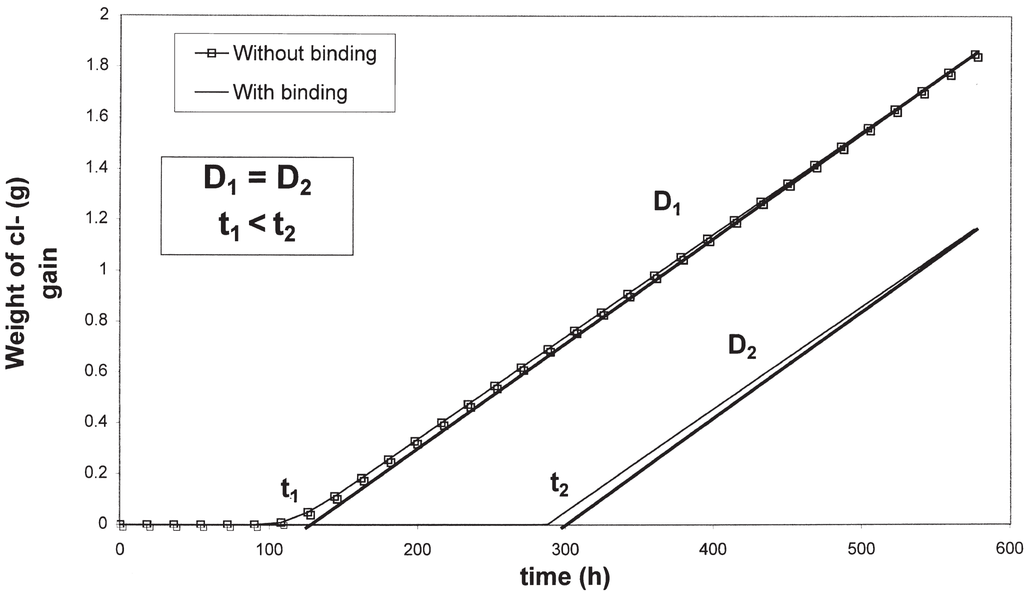

Fig. 3. Migration test simulation (D_e=2.10^{-12} m^2/s, thickness=1cm, c_{up}=0.564mol/L, U=12V).

occur at the anode: 2 Cl^- (aq) $\rightarrow$ Cl_2 (g) + 2 e^- and 6 H_2O (l) $\rightarrow$ O_2 (g) + 4 H_3O^+ (aq) + 4 e^-.

These reactions depend mainly on the electrode potential, the intensity in the circuit, and the upstream solution pH [9]. We can easily understand that we must avoid the first reaction, otherwise a part of the chloride ions that reach the anode disappears as gaseous chlorine Cl_2(g). The measurement of the flux and therefore of the diffusion coefficient will be wrong. This phenomenon can be observed essentially when the tested concrete is cracked or very porous. Indeed, as the conductivity of the concrete sample increases, the intensity in the circuit becomes larger and the solution becomes acidic and this favors the formation of chlorine Cl_2(g).

On the other hand, if the medium remains basic with a high pH, we can see in Fig. 4 that chloride ions are not the only species in the solution [10]. Hypochlorite ions ClO^- can be present in the anodic solution as well. Their amount depends essentially on the pH, the electrode potential, and therefore, once again, the concrete conductivity. Those ions may disturb the measurements during the titration of the downstream solution.

Indeed, if a titrimetric method with silver nitrate is used,

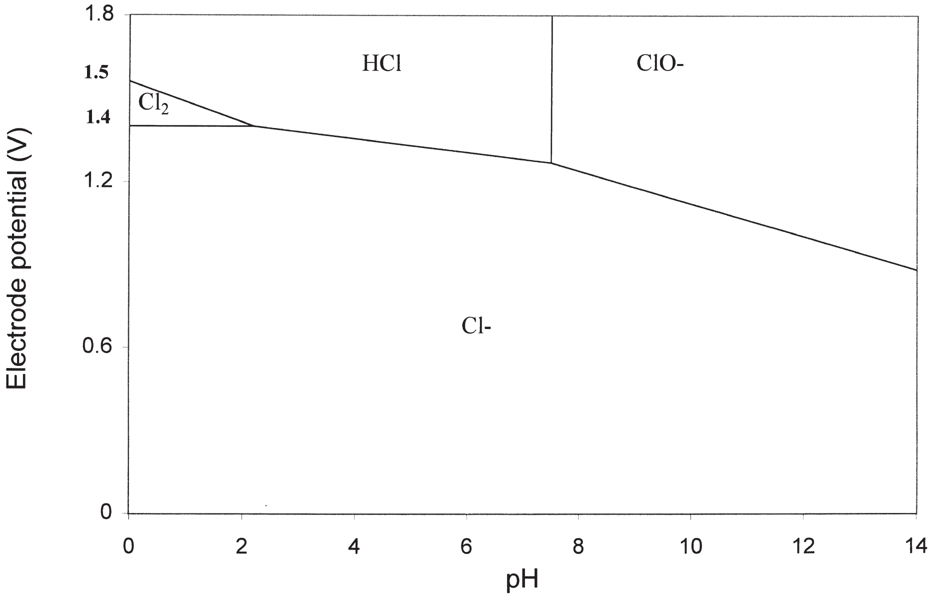

Fig. 4. Potential-pH diagram for Cl [10].

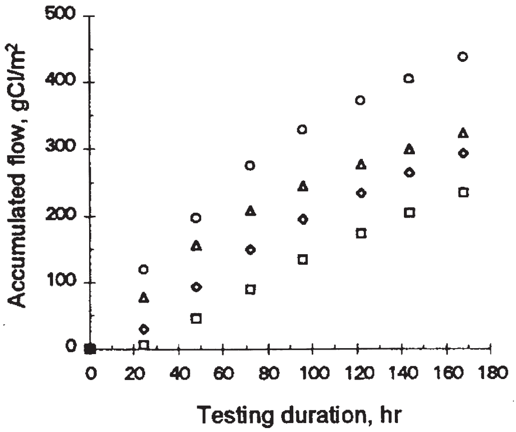

Fig. 5. Steady state migration tests [6].

acid must be added to the solution to make the titration possible. This acid will react with hypochlorite ions according to the following reaction: $ClO^- (aq) + Cl^- (aq) + 2H^+ (aq) \rightarrow Cl_2 (g) + H_2O (l)$. Therefore, we can see that one part of the chloride ions will not be measured because they will disappear as gaseous chlorine.

We can see very well the influence of these problems if we observe some results published by Tang [6]. Fig. 5 shows the accumulated flow of chloride ions in the downstream cell for concrete with different water/cement ratios. We can notice that after 80 h there is an obvious decrease in the measured flux for concretes with water/cement ratio > 0.5. According to Tang, for those concretes the effective diffusion coefficient from steady-state tests and the diffusion coefficient from non-steady-state tests lead to different intrinsic diffusion coefficients D_0. The chemical reactions at the anode and the errors made during the titration of the downstream solution could explain such a difference. Indeed, as the amount of chloride ions in the downstream cell is underestimated, the intrinsic diffusion coefficient obtained from the effective diffusion coefficient is certainly wrong.

Therefore we stress the fact that the procedure to determine the effective diffusion coefficient from the measurement of the chloride ion concentration in the downstream cell is not perfect. Indeed, the durations of the tests can be important, the experiments can be difficult to perform, and finally the value of the diffusion coefficient is determined with varying degrees of accuracy depending on the procedure that is used.

To make up for these difficulties, we present in this article a new method that permits the determination of the effective diffusion coefficient. We show that it is not necessary to measure the chloride ion concentration in the downstream cell and that it is more judicious to measure the drop in chloride concentration in the upstream cell. We can obtain effective diffusion coefficients very quickly while keeping the possibilities offered by the steady-state migration test:

Measurement of D_e variation with the concentration
D_e measurement when the sample is already contaminated with chloride ions

and so on.

2. Theoretical approach

During diffusion tests or migration tests we determine the time necessary to reach the steady state by following the increase in the chloride concentration in the downstream solution. Another possibility could consist of measuring the drop in the upstream concentration. We are going to discuss from a theoretical point of view these two different approaches both for a diffusion process and for a migration process.

2.1. Diffusion

In the case where the diffusing species and the concrete do not interact, we can easily show [11] that the accumulated loss of chloride ions Q_{up} in the upstream cell in the non-steady state is equal to [cf. Fig. 6; see Eq. (3)]:

$$Q_{\mathrm{up}}(t) = 2Sc_{\mathrm{up}}\left(\frac{pD_e t}{\pi}\right)^{\frac{1}{2}} \tag{3}$$

where

c_{up}: upstream concentration (mol/m^3)
p: porosity
t: time (s)
S: surface of concrete exposed to the chloride solution (m^2)

The steady state is reached for a time equal to the time lag t_l defined by Massat [12] according to the relation shown in Eq. (4):

$$t_l = \frac{pL^2}{6D_e} \tag{4}$$

where
t_l: time lag (s)
L: thickness of the sample (m)

The chloride ion flux through the sample becomes constant and we end up with Eq. (5):

$$J_{\mathrm{up}} = J_{\mathrm{down}} = D_e\frac{C_{\mathrm{up}}}{L} \tag{5}$$

This is the classical Fick's first law with:

J_{up}: upstream flux of chloride ions (mol/m^2/s)
J_{down}: downstream flux of chloride ions (mol/m^2/s)

If the chloride ions and the concrete interact, we can show [11] that the time lag $t_{l,\mathrm{bind}}$ can be expressed as shown in Eq. (6):

$$t_{l,\mathrm{bind}} = t_l\left[1 + \left(\frac{1-p}{p}\right)\rho_s\frac{\partial C_b}{\partial c}\right] \tag{6}$$

where

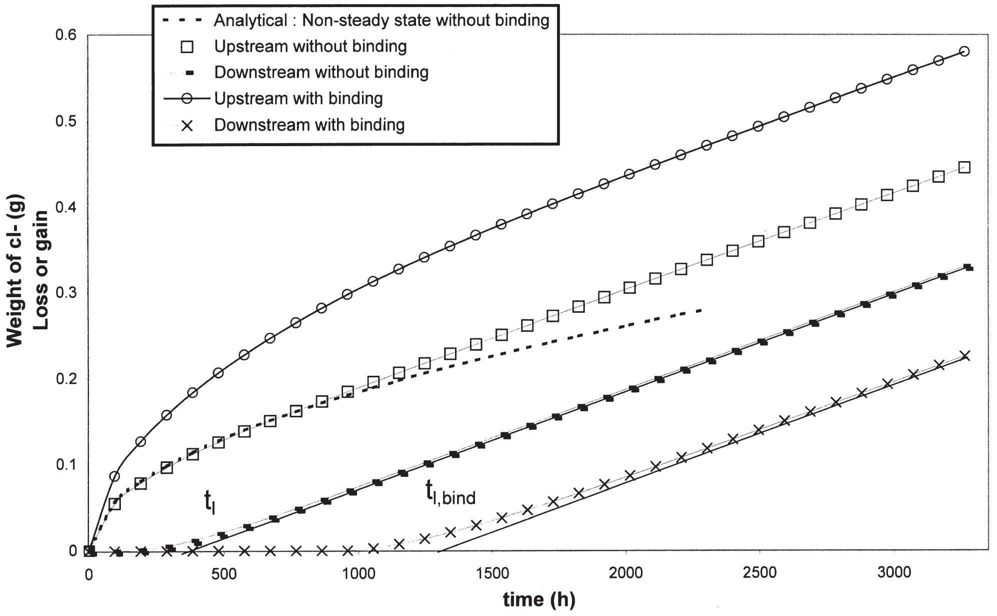

Fig. 6. Simulated quantity of Cl^- ions upstream (loss) and downstream (gain) ($D_e = 2.10^{-12} m^2/s$, $L = 1 cm$, $c_{up} = 0.564 mol/L$).

ρ_s: density of dry material (kg/m^3)
C_b: bound chlorides (mol/kg)
c: free chlorides (mol/m^3)

We have consequently [see Eq. (7)]:

$$t_l < t_{l,\text{bind}} \tag{7}$$

Therefore the steady state is reached later than in the previous case because the interactions slow down the chloride ions penetration. However, when the steady state is established, the flux remains constant within the concrete and identical to the one given by Eq. (5). The effective diffusion coefficient is therefore independent of interactions.

To summarize, we can say that whether we calculate the effective diffusion coefficient from the upstream flux or from the downstream flux of chloride ions, we will obtain the same result during the steady state. The time to reach the steady state upstream or downstream is the same so usually we measure the flux in the downstream cell but we could measure the upstream flux as well. In the diffusion test, there are two principal reasons why we measure the chloride concentration in the downstream compartment. First, it allows us to quantify the interactions between the chloride ions and the concrete [13], and the chloride concentration analysis is easier to perform downstream.

2.2. Migration and diffusion of chloride ions

Let us now examine the case of a migration process coupled with the diffusion process. We know from Eq. (1) that the flux of ions through a saturated concrete sample, where the convection term can be ignored, can be written as seen in Eq. (8):

$$-\mathrm{J}(x) = D_e\frac{\partial c}{\partial x} + \frac{zF}{RT}D_e cE \tag{8}$$

During a migration test, assuming that the upstream side of the concrete sample will be very quickly saturated with chloride ions, we can neglect the diffusion term since there will be no concentration gradient at $x = 0$ (cf. Fig. 7). Therefore, the flux of chlorides through the upstream side is constant and equal to [see Eq. (9)]:

$$\mathrm{J}_{\mathrm{up}} = \frac{F}{RT}D_{e,\mathrm{up}}c_{\mathrm{up}}E \tag{9}$$

We can see that the upstream flux is independent of interactions and time. The calculated curves in Fig. 8 show that the effective diffusion coefficient can be determined very quickly from the flux through the upstream side of the concrete sample. Indeed, it is not necessary to wait for the steady state to be established as in the case of the flux measurement in the downstream cell.

If all the parameters for the tests are well controlled (potential difference, temperature) we can then determine the effective diffusion coefficient by measuring the drop in chloride ion concentration in the upstream cell. It is only necessary to apply Eq. (10):

$$D_{e,\mathrm{up}} = \frac{1}{c_{\mathrm{up}}}\frac{RT}{F}\frac{\mathrm{J}_{\mathrm{up}}}{E} \tag{10}$$

where

E: electrical field (V/m)
J_{up}: chloride ion flux through the upstream side of the sample (mol/m^2/s)
c_{up}: average concentration in the upstream cell (mol/m^3)

With [see Eq. (11)]:

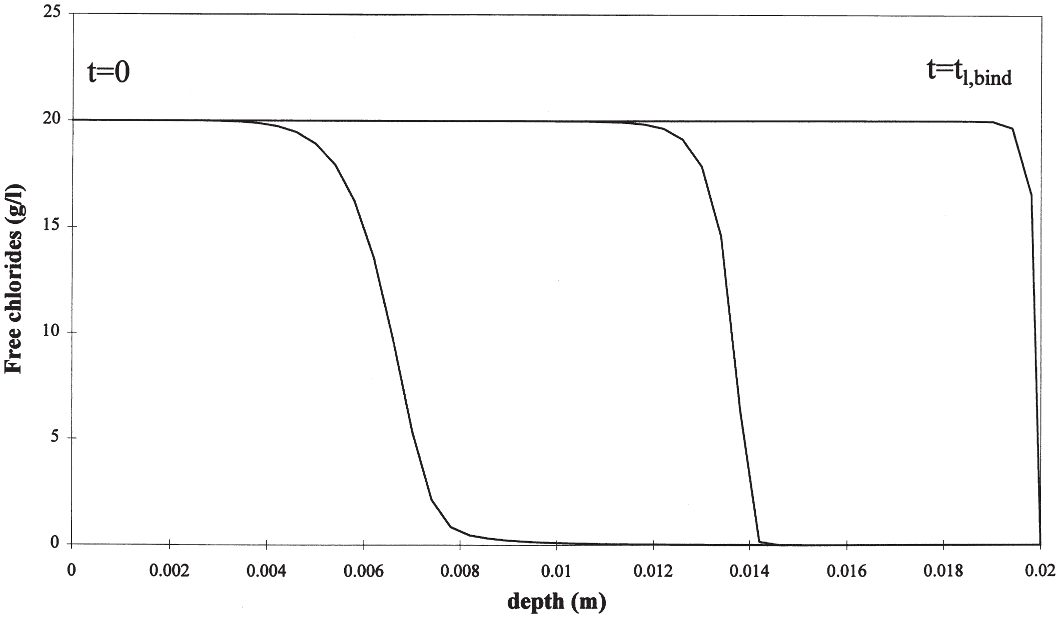

Fig. 7. Simulated concentration profiles of Cl$^-$ ions ($D_e=2.10^{-12}m^2/s$, L=1cm, $c_{up}=0.564mol/L$, U=12V).

$$J_{up} = \frac{c_{up1}V - c_{up2}V}{St} \tag{11}$$

where

c_{up1}: concentration at the beginning of the test (mol/m^3)
c_{up2}: concentration at the end of the test (mol/m^3)
V: volume of solution in the upstream cell (m^3)
S: concrete surface exposed to chloride ions (m^2)
t: duration (s)

Starting from Eqs. (2) and (11), we can then compare the values of the effective diffusion coefficients for the same concrete sample, by measuring the upstream and downstream flux of chlorides.

3. Experimental study

3.1. Procedure and concrete composition

Four different concretes were made in accordance with the French NFP18305 standard, which specifies conditions to ob-

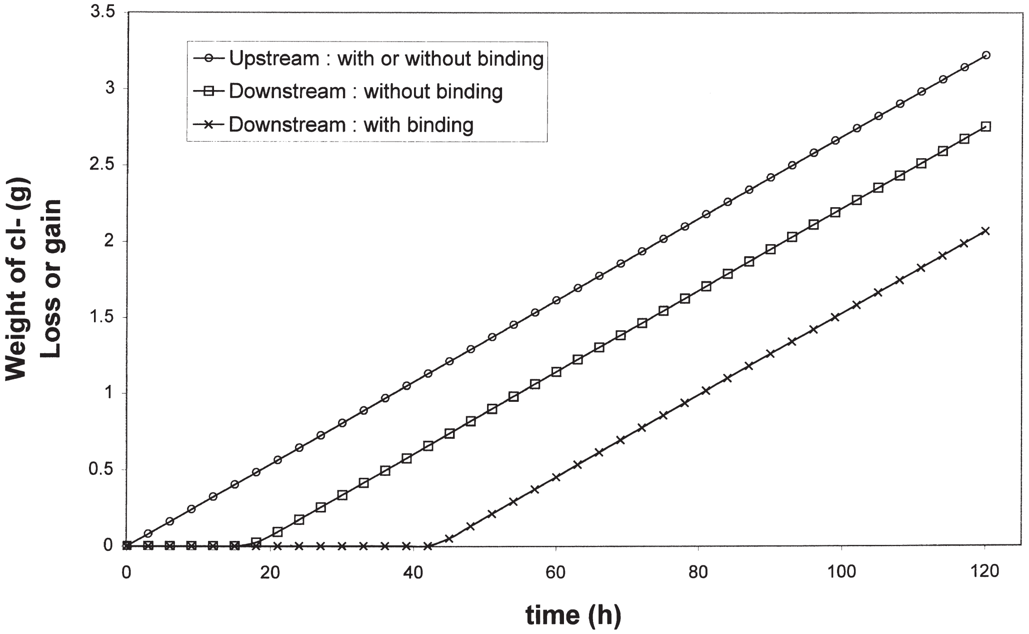

Fig. 8. Simulated upstream and downstream flux during a migration test ($D_e=2.10^{-12}m^2/s$, L=1cm, $c_{up}=0.564mol/L$, U=12V).

Table 1
Concrete characteristics

	Water/cement ratio			
	0.32	0.32	0.55	0.55
Cement dosage (kg/m^3)	CPA-CEMI 52,5 PMES 425	CPA-CEMI 52,5R 425	CPA-CEMI 52,5 PMES 364	CPA-CEMI 52,5R 364
Gravel 10/14 (kg/m^3)	730	730	690	690
Gravel 4/10 (kg/m^3)	400	400	372	372
Sand 0/4 (kg/m^3)	750	750	708	708
Water (L/m^3)	136	136	200	200
Superplasticizer (% cement)	2	2	–	–
28-d compressive strengh (MPa)	72	92	33.5	34.5
28-d porosity (%)	11.2	11.2	16.5	17.3

serve when the concrete structure is located in a marine environment. Two kinds of cement were studied for two different water/cement ratios. The porosity to water and the 28-day compressive strength of these concretes have also been determined. The characteristics of these concretes are shown in Table 1. The chemical composition of the cements is shown in Table 2.

For each concrete, we cast cylindrical samples (∅11 × 22 cm). From those samples, we cut 3-cm thick discs. Before the migration tests, these discs were vacuum-saturated with a basic alkaline solution (NaOH + KOH). The concretes were tested after 14 days of standard water curing and 1 day of preconditioning. The times given in Figs. 9, 10, and 11 do not include these 14+1 days prior to testing. The downstream solution was changed every 2 to 3 days and the upstream solution every 5 to 7 days. These changes are necessary for the titration of the solutions but they also permit a basic pH to be obtained in the downstream cell. The tests lasted about 15 days. This duration is sufficient to reach the steady state and it allows us to make two or three measurements of the flux in the upstream cell. A 12-V voltage was applied between the sides of the concrete sample, and it was checked throughout the test. The solutions were titrated with silver nitrate (0.1 M). For upstream solutions, small amounts (0.5 mL) were taken with an electronic pipette. Therefore the solutions have not been diluted and this improved the accuracy of the measurements. The solutions were made with NaOH (0.025 mol/L) + KOH (0.083 mol/L) in upstream and downstream cells. NaCl (0.564 mol/L) was added in the upstream solution.

3.2. Results

The variation over time in the quantity of chloride ions in the upstream and downstream cells is shown in Fig. 9 for concretes with water/cement ratios equal to 0.32. Figs. 10 and 11 show the variation over time of the effective diffusion coefficient determined from upstream data.

4. Discussion

4.1. Influence of binding

It can be seen in Fig. 9 that the flux measured in the upstream and downstream cells is equal once the steady state is established. The simulated curves shown in Fig. 8 are confirmed and we clearly demonstrate that the upstream flux is independent of interactions between chloride ions and concrete. Therefore, it is correct to calculate the effective diffusion coefficient from Eq. (10).

4.2. Influence of time and concrete mixture

We can notice in Figs. 10 and 11 that the variation of the effective diffusion coefficient $D_{e,\mathrm{up}}$ depends on time and concrete mixture. For the concretes with water/cement ratios = 0.55, $D_{e,\mathrm{up}}$ decreases drastically between 15 and 30 days, whereas for concrete with water/cement ratios = 0.32 the values are almost constant. This is a logical result that confirms permeability data or cement hydration theories [14].

Therefore, to compare $D_{e,\mathrm{up}}$ and $D_{e,\mathrm{down}}$ we have to be very careful. Fig. 12 shows the simulated flux upstream and downstream during a migration test. The duration of this simulated test was 10 days. For the purpose of the simulation, we made the effective diffusion coefficient vary linearly with time for 5 days and then we kept it constant. This simulation demonstrates why it is important to calculate $D_{e,\mathrm{up}}$ and $D_{e,\mathrm{down}}$ once the steady state is reached to avoid the influence of the variation of the diffusion coefficient.

Fig. 13 shows a comparison between the values of the effective diffusion coefficient measured from upstream and downstream data for the different concretes. To neglect the concrete age effect and therefore the variation of the effective diffusion coefficient, the value $D_{e,\mathrm{up}}$ for $t = 4$ days was not taken into account in calculating the average value from upstream data.

Table 2
Chemical composition of cements (%)

Cement	Na_2O	K_2O	Cl	CaO	SO_3	SiO_2	Al_2O_3	MgO	Fe_2O_3	LOI
CPA-CEMI 52,5 PMES	0.29	0.10	0.05	67.2	2.1	22.7	2.9	0.71	2.0	1.79
CPA-CEMI 52,5R	0.12	0.62	0.05	63.2	2.96	19.7	5.25	1.89	2.28	1.78

LOI = loss on ignition.

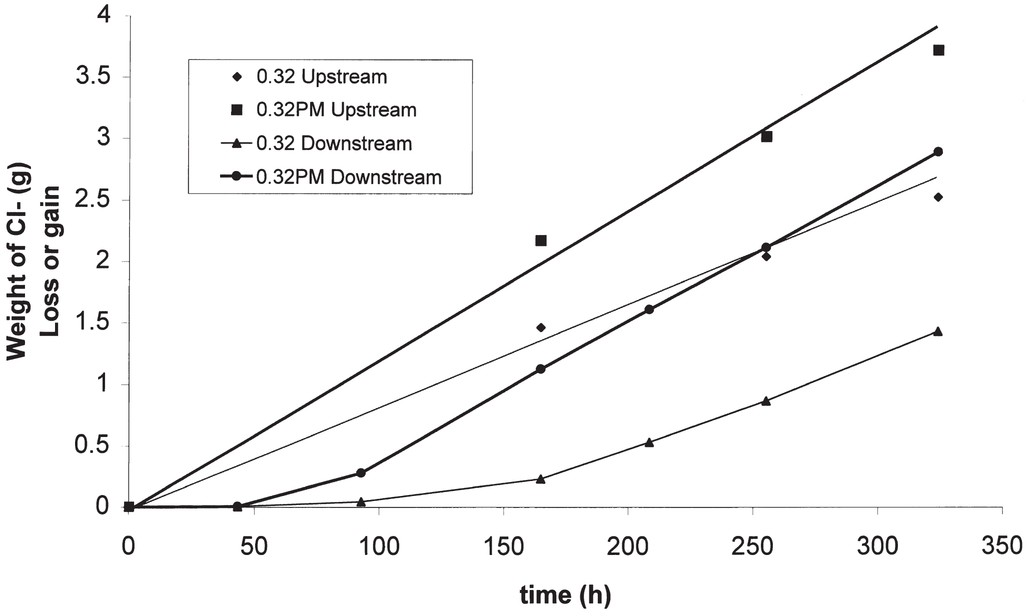

Fig. 9. Experimental flux upstream and downstream during a migration test.

It can be seen that the results confirm the theory. Indeed, the measured diffusion coefficients from upstream data are equal to the diffusion coefficients measured from downstream data. Concerning the concretes with water/cement ratios = 0.55, the accuracy would have been better if the concrete microstructure had been stable during the test. Nevertheless, the determination of the effective diffusion coefficient from the measurement of the upstream flux is correct. Indeed, we can obtain a diffusion coefficient with the same accuracy if the flux is measured downstream, but in that case it is not necessary to wait for the steady state to be established. Moreover, in this way the problems related to chemical reactions that can occur at the anode are avoided.

It must also be emphasized that when we have to calculate $D_{e,\mathrm{down}}$ from Eq. (2), we need to know the concentration upstream. Usually, this concentration is assumed constant, but to obtain the exact diffusion coefficient downstream this value should be known during the test.

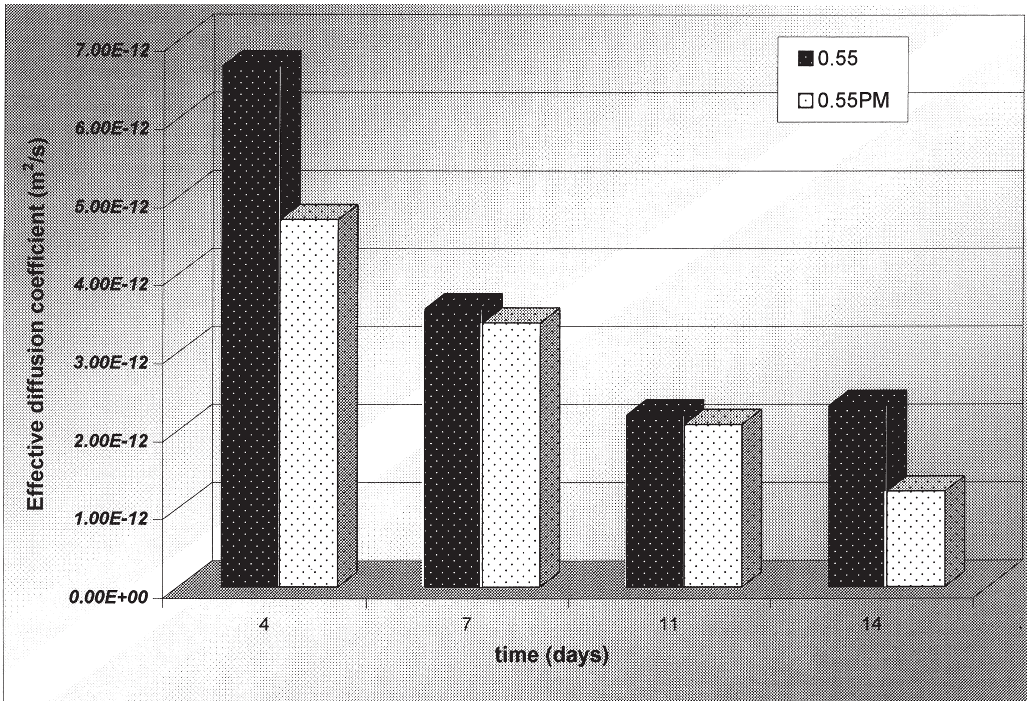

Fig. 10. $D_{e,\mathrm{up}}$ values from upstream data for concretes with W/C=0.55.

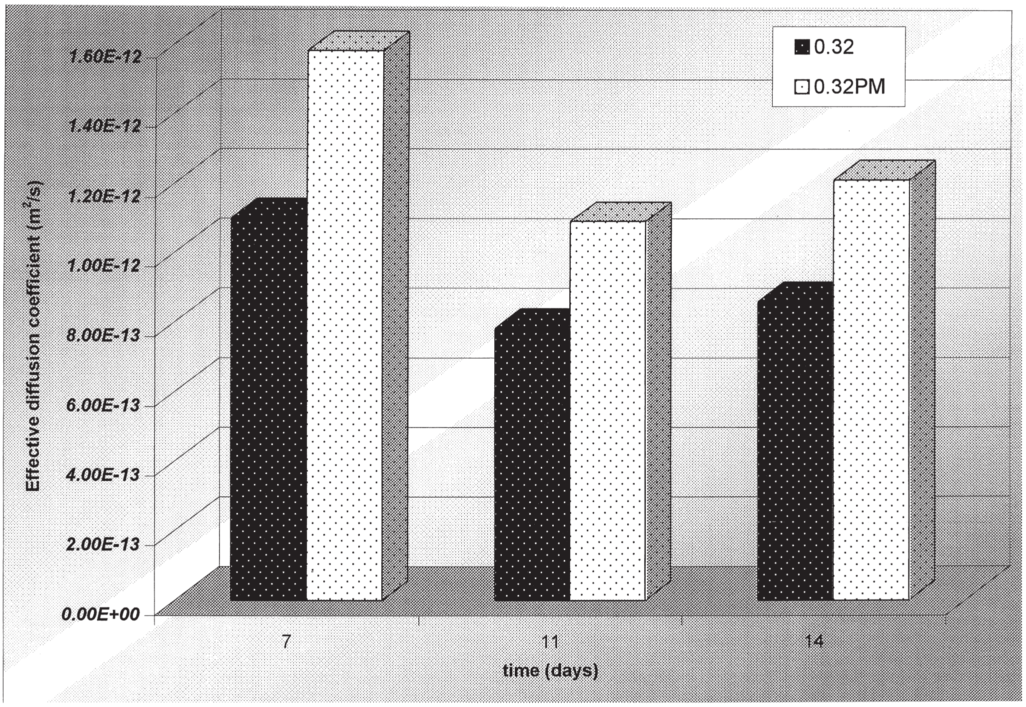

Fig. 11. $D_{e,up}$ values from upstream data for concretes with W/C=0.32.

Finally, it must be noticed that it is not possible to obtain the variation of the effective diffusion coefficient when the concrete is very young by measuring $D_{e,\text{down}}$. Only a rapid method can determine this variation with good accuracy.

5. Conclusions

Measurement of the coefficient $D_{e,\text{down}}$ is long and the tests are not easy to perform. Moreover, chemical reactions can occur at the anode. Those reactions are difficult to control and to quantify. The value of the diffusion coefficient is therefore determined with a large uncertainty.

The measurement of the flux of chloride ions through the upstream side of a concrete sample allowed us to highlight the following points:

- The upstream flux is constant and therefore independent of interactions.

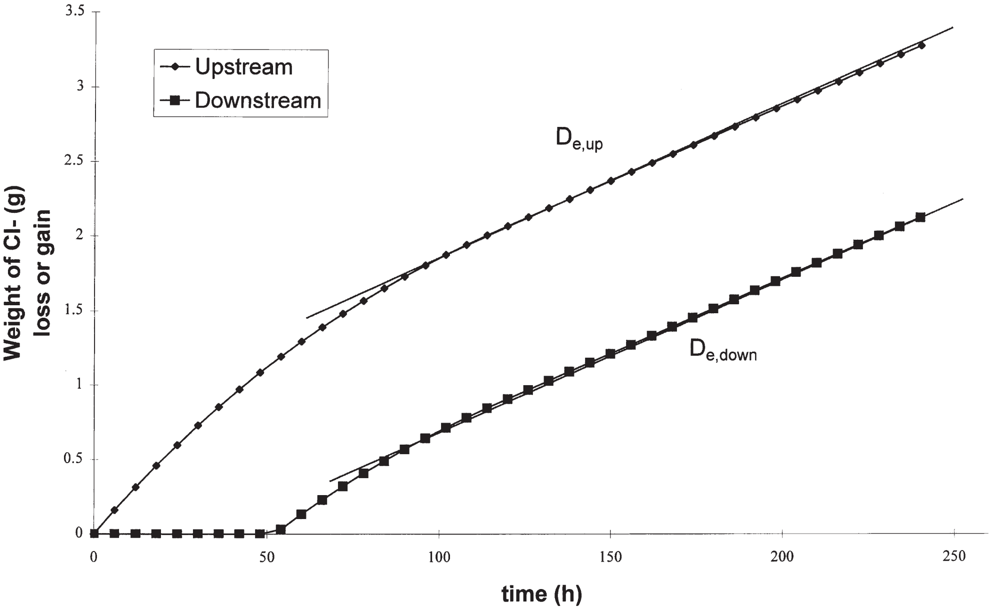

Fig. 12. Simulation of a migration test—Influence of the variation of the effective diffusion coefficient with time (L=1cm, c_{up}=0.564mol/L, U=12V).

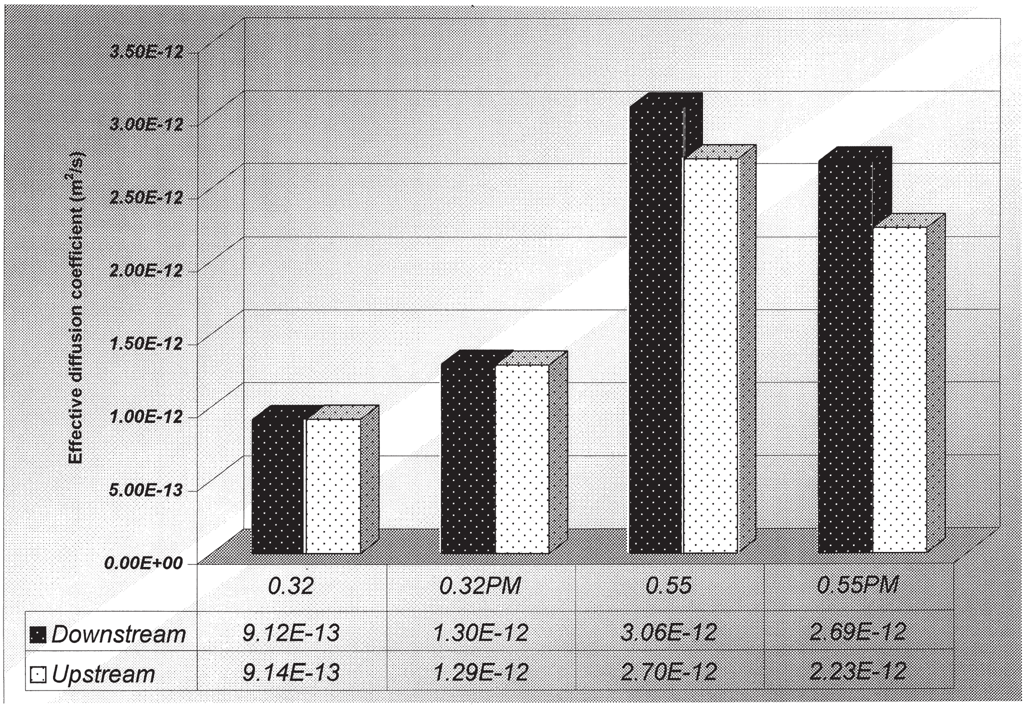

Fig. 13. Comparison between $D_{e,up}$ and $D_{e,down}$.

- The diffusion coefficient $D_{e,\mathrm{up}}$ is equal to the diffusion coefficient $D_{e,\mathrm{down}}$.

The effective diffusion coefficient can be determined with the same accuracy but faster than before. This method is currently used in our laboratory and should allow us to quantify the influence of different parameters such as the age of the concrete and the chloride ion concentration on the effective diffusion coefficient. The relations will then be introduced in a predictive model for the rate of chloride ion penetration in a reinforced concrete structure.

Eventually, it may also be possible to use this method to measure the diffusion coefficient of concretes already contaminated by chloride ions.

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