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PREDICTION OF DIFFUSION COEFFICIENTS IN CEMENT-BASED MATERIALS ON THE BASIS OF MIGRATION EXPERIMENTS

A. Delagrave, J. Marchand and E. Samson
Concrete Canada and Centre de Recheche Interuniversitaire sur le Béton (CRIB)
Université Laval, Ste-Foy, Québec, Canada, G1K 7P4

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Abstract

The chloride diffusion and migration coefficients of 15 different mortar mixtures were systematically compared. Test parameters included water/binder ratio (0.25 and 0.45), type of binder (ASTM type I, ASTM type III, and ASTM type V), use of silica fume and sand volume fractions (0%, 30%, and 50%). Test results indicate the various ways of evaluating chloride transport coefficients generally yield much different values. Test results also show that the assumption of non interacting diffusing flows, used in the mathematical treatment of diffusion and migration equations, is most probably incorrect.

Introduction

In northern countries, the corrosion of reinforcing steel is, by far, the main cause of the premature deterioration of highways and marine structures. In the past decade, numerous surveys have clearly indicated that chloride ions, originating from deicing salts or sea water, are the primary cause of reinforcing steel corrosion [1]. The chloride ions that penetrate through the concrete cover depassivate the oxide film covering the reinforcing steel and accelerate the reaction of corrosion. Most studies tend to indicate that chlorides are transported through the concrete pore network and microcracks by a diffusion process [1].

Most of the laboratory diffusion experiments actually carried out are generally time consuming. Simple steady-state diffusion tests and immersion tests can last several months. In order to obtain rapid information on the ability of a concrete structure to resist chloride ion ingress, numerous attempts to design accelerated test procedures have been made. In most cases, the transport of ions through the samples is accelerated by applying an electrical potential [2-4]. However, there exists very little information on the ability of these accelerated procedures to reliably predict the penetration of chloride ions into cementitious systems.

The only systematic comparison between non-accelerated and accelerated test methods has been carried out by Tang [5]. The author compared coefficients derived from non-steady state diffusion tests to others obtained from non-steady state migration experiments. The two series of coefficients were found to correlate reasonably well. As pointed out by the author himself, the good correlation between the two series of results is however a little surprising considering that the strong ion/hydrated cement paste interactions taking place during the diffusion experiment were not accounted for in the calculations of the coefficient.

The present investigation was carried out to evaluate the ability of migration tests to reliably predict the diffusion coefficient of chlorides in cement-based materials. The investigation was carried out as part of more comprehensive research program aimed at studying the long-term durability of high-performance concrete structures exposed to chloride solutions [6].

Test Program

Five different series of mixtures were cast. Each series was made of a different type of binder. For each series, three mixtures of variable sand volume fractions were prepared (0%, 30%, and 50%). The chloride binding capacity of the neat paste samples of each series of mixtures was determined. The transport properties of chloride ions were assessed using two different experimental procedures: an unsteady-state diffusion test (immersion test) and a steady-state migration test where the movement of chloride ions was accelerated under electrical potential.

Data obtained from these two test series served as a basis for the calculation of various chloride transport coefficients. An apparent diffusion coefficient was determined according to the penetration profile data. A numerical model was developed to determine the effective diffusion coefficient on the basis of the chloride ion penetration profiles and the chloride binding isotherms. Two different migration coefficients were derived from the flow of chloride ions passing through the sample and the current density. Another migration coefficient was determined taking into account the ionic interactions according to the equation developed by Zhang and Gjorv [7].

Materials and Mixture Characteristics

Two water/binder ratios were used in the preparation of the five series of mixtures. The water/binder ratio of the first two series was fixed at 0.25 while that of the three remaining series were prepared at a water/binder ratio of 0.45. The binder used in the preparation of the two 0.25 water/binder ratio series was an ASTM type III cement. Silica fume (6 wt%), used as partial cement replacement, was added to one of the series. Two of the three 0.45 water/binder ratio series were prepared with an ASTM type I cement. Silica fume (6 wt%), used as partial cement replacement, was added to one of the series. The last 0.45 water/binder ratio series was prepared with an ASTM type V cement. The chemical analyses of the cements are given in Table 1.

For each of the five series, three different mixtures were prepared. The sand volume fractions of each of the three mixtures were respectively 0%, 30% and 50%. A standardized crushed siliceous sand (Ottawa sand ASTM C-109) having a density of 2.60 was used in the preparation of all mixtures. For the 0.25 water/binder ratio series of mixtures (with and without silica fume), a melamine-based superplasticizer was used at a dosage of 2.1% of dry material by mass of cement. The composition of all mixtures is summarized in Table 2.

Two 2.5 × 2.5 × 11 cm prisms for each mixture were cast to study the chloride ion penetration. All samples were cured for 2 months in a saturated lime solution. All specimens for the migration experiments were cast in plastic molds (diameter = 9.5 cm, height = 20 cm). The molds were sealed and rotated for the first 24 hours to prevent segregation. At the end of this period, the specimens were demolded and immersed in a saturated lime solution

TABLE 1

Chemical and Mineralogical Composition of the Cements

Chemical analysis (%)	ASTM I	ASTM III	ASTM V
Silicon dioxide (SiO_2)	20,09	20,48	22,29
Aluminium trioxide (Al_2O_3)	3,87	4,03	3,48
Ferric trioxide (Fe_2O_3)	1,69	1,78	4,37
Calcium oxide (CaO)	63,82	64,73	63,92
Sulfur trioxide (SO_3)	3,50	3,33	2,19
Magnesium oxide (MgO)	2,22	2,31	1,42
Sodium oxide (Na_2O)	0,30	0,36	0,22
Potassium oxide (K_2O)	0,39	0,34	0,70
Titanium dioxide (TiO_2)	0,16	0,17	0,18
Manganese oxide (MnO)	0,05	0,05	0,08
Bogue Composition			
C_3S	68,7	68,7	54,9
C_2S	5,8	6,9	22,5
C_3A	7,4	7,7	1,8
C_4AF	5,1	5,4	13,3
Physical properties			
Blaine (cm^2/g)	4616	5351	3800

for a 3-month period. The temperature of the curing baths was kept approximately constant at 21° C.

Experimental Procedures

Chloride Binding Isotherms. Chloride binding isotherms were determined for the neat paste samples of each series of mixtures according to the procedure described by Tang and Nilsson [8]. The chloride binding isotherms for the five paste mixtures in the present investigation were presented in chapter 5 of this document (see section 5.2).

Chloride Ion Penetration Profiles. The apparent diffusion coefficient was determined by measuring the total chloride ion penetration profile of the prisms. Prior to the immersion in the chloride solution (30 g/l of NaCl), all the surfaces of the prisms were coated with wax except one end (2.5 × 2.5 cm^2) to promote a unidirectional penetration. The samples were immersed in the solution for a 12-month period. The temperature was kept constant at 21°C throughout the entire test period. At the end of the immersion period, the prisms were dry sawed in 5-mm thick pieces. Each piece was first ground to pass the 820 μm sieve. The acid soluble chloride content of the powders was determined according to ASTM C1152.

Steady-State Migration Tests. The chloride ion migration coefficient was determined using a migration test. Discs of 95 mm in diameter and 15 mm thick were used for the migration experiments. All discs were immersed in deionized water and vacuum saturated for 24 hours prior to testing. The discs were then mounted on the migration cells for testing. The migration cells used in this study are similar to the one described by El-Belbol and Buenfeld [3]. Contrary to their experimental set-up, both compartments of the cells were equipped with an agitating device in order to maintain the homogeneity of the solutions, and ruthenium-coated titanium electrodes were used. The upstream compartment of each cell was filled with a 12 g/l (0.3 M) sodium hydroxide solution containing 30 g/l of sodium chloride (0.5 M). The downstream compartment of each cell was filled with a 12 g/l (0.3M) sodium hydroxide solution.

A voltage of 10 V was applied on each cell, and the temperature of the cells was kept constant at 21°C throughout the entire duration of the tests. The chloride concentration of the solution in the downstream compartment was determined at regular intervals by means of potentiometric titration using a silver nitrate electrode. Two duplicate specimens were tested. The experiments lasted approximately 3 weeks. The current passing through the sample was also monitored at regular intervals throughout the test period.

Theoretical Considerations

Apparent Diffusion Coefficient (D_{F2}). The Fick's second law of diffusion (eq. 1) was used to evaluate the apparent chloride ion diffusion coefficient.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D_{F2}\frac{\partial C}{\partial x}\right) \tag{1}$$

The diffusion coefficients were calculated according to the well-known solution of Fick's second law of diffusion (eq. 2), which has been derived from eq. 1, assuming a constant

TABLE 2

Mixture Compositions

Mixture	W/B	Cement	Silica fume (%)	Sand volume (%)
M25-0	0.25	ASTM III	0	0
M25-30	0.25	ASTM III	0	30
M25-50	0.25	ASTM III	0	50
M25(FS)-0	0.25	ASTM III	6	0
M25(FS)-30	0.25	ASTM III	6	30
M25(FS)-50	0.25	ASTM III	6	50
M45-0	0.45	ASTM I	0	0
M45-30	0.45	ASTM I	0	30
M45-50	0.45	ASTM I	0	50
M45(FS)-0	0.45	ASTM I	6	0
M45(FS)-30	0.45	ASTM I	6	30
M45(FS)-50	0.45	ASTM I	6	50
MQ50-0	0.45	ASTM V	0	0
MQ50-30	0.45	ASTM V	0	30
MQ50-50	0.45	ASTM V	0	50

diffusion coefficient. The values of the apparente diffusion coefficient were determined from a statistical analysis of the penetration data of each mixture. The values of D_{F2} thus calculated were those that best fitted the penetration profiles.

$$\frac{C_s - C_x}{C_s - C_0} = \operatorname{erf}\left(\frac{x}{\sqrt{4D_{F2}t}}\right) \qquad (2)$$

where C_s is the chloride concentration of the sample at the surface, C_x the chloride concentration of tha sample at a depth x, C_0 the initial chloride concentration of the mortar before immersion in a chloride solution ($C_0 = 0$), t the time of exposure, D_{F2} the apparent diffusion coefficient, and erf the error function.

Effective Diffusion Coefficient (D_{F1}). As described in chapter 6 (see section 6.2.2) of this document, the Fick's second law of diffusion has to be solved numerically because of the non linearity of the chloride binding capacity which implies that the apparent diffusion coefficient is probably not constant. The finite element method was used in the development of a numerical model to solve the Fick's second law of diffusion. The relationship proposed by Nilsson et al. [9] linking D_{F2} and D_{F1} (equation 3) was used in the simulations.

$$D_{F2} = D_{tot} = \frac{D_{F1}}{p_{sol}\left[1 + \frac{\partial C_b}{\partial C_f}\right]} \qquad (3)$$

where psol is the porosity of the material, and $\frac{\partial C_b}{\partial C_f}$ is the binding capacity which is the slope of the binding isotherm.

The test results of the binding isotherms, presented in section 5.2 of this report, clearly indicate that the binding isotherms can be well represented by a Freundlich isotherm:

$$\log C_b = a \log C_f + b \qquad (4)$$

Table 3 presents the equations of the Freundlich isotherms for all the paste mixtures. As can be seen, the use of a Freundlich isotherm appears to yield good results, the correlation coefficient being at least 98%.

Migration Coefficients. The first migration coefficient was obtained by measuring the total flow of chloride ions passing through the mortar sample. The migration coefficient (M) was evaluated according to equation (5):

$$J = J_{diff} + J_{el} = -D\frac{\partial C}{\partial x} + MzC\frac{FE}{RT} \qquad (5)$$

where J represents the flux of chlorides migrating through the sample, J_{diff} the flux of chloride ions originating from diffusion, J_{el} the flux of chloride ions originating from the electrical field, D the chloride ion diffusion coefficient, $\frac{\partial C}{\partial x}$ the concentration gradient, z the ion valency (−1 in the case of chlorides), F the Faraday constant, E the external electrical field

TABLE 3

Freundlich Isotherms Characteristics for the Paste Mixtures

Mixture	a	b	r^2
M25-0	0,4642	0,936	0,985
M25(SF)-0	0,4772	0,814	0,981
M45-0	0,5133	1,048	0,992
M45(SF)-0	0,4982	1,004	0,994
M45(50)-0	0,4757	1,037	0,997

applied on the system, R the gas constant, T the temperature in Kelvin, and c the chloride concentration in the upstream compartment. For an applied voltage of 10 V, the total flux of chlorides passing through the sample is probably mainly driven by the electrical potential gradient, and the first term of equation (5) can therefore be neglected in the calculations.

As explained by Bockris and Reddy [10], when an external electric field is applied to a population of ionic species, some ionic species migrate more than others. Even if there are equal numbers of the various ions, those which have higher mobility contribute more to the transport of the current. The fraction of current carried by one specific ionic species is called the transport number (t_i):

$$t_i = \frac{i_i}{i} = \frac{|z_i|\lambda_i C_i}{\sum |z_i|\lambda_i C_i} \tag{6}$$

where i the total current applied to the system, i_i the fraction of the total current carried by the ionic species, λ_i is the molar conductivity, z_i the ion valency, C_i the ionic concentration of the species.

According to Bockris and Reddy [10], the electrical component $(J_i)_{el}$ of the total flux is proportional to the fraction of current carried by the ionic species under study:

$$\left(\vec{J}_i\right)_{el} = \frac{i t_i}{|z_i| F} \tag{7}$$

As suggested by Andrade [11], by replacing equation 7 in equation 5 and assuming that the diffusion flux is negligible compared to the migration flux, one obtains the following relationship which is similar to the Nernst-Einstein relation:

$$D_i = \frac{RT}{z_i F^2}\lambda_i = \frac{i t_i}{z_i^2 F}\frac{RTL}{\psi C_0 F} \tag{8}$$

As previously stated, the current density was measured throughout the entire test period of the migration experiments. According to equation 8, it is possible to calculate a conduction coefficient (M_{cond}) using the steady-state regime current value. Because of the lack of information concerning the influence of the solution composition on its conductivity, all transport numbers were calculated assuming no ion/ion interaction (hypothesis of a ideal solution) in accordance with equation (6). The molar conductivity of each species can be found in several text books ($\lambda^0_{Cl^-} = 76,4\Omega^{-1}cm^2mol^{-1}$; $\lambda^0_{Na^+} = 50,1$; $\lambda^0_{OH^-} = 197,6$).

Assuming that, in a steady-state regime, the composition of the pore solution is similar to that in the upstream compartment, one finds that, for the solution used in this experiment (0.5 mol/l NaCl and 0.3 mol/l NaOH), the theoretical transport number is:

$$t^{Cl-}_{theo} = \frac{|z_{Cl-}|\lambda_{Cl-}C_{Cl-}}{\sum |z_{Cl-}|\lambda_{Cl-}C_{Cl-}} = \frac{0,5(76,4)}{0,5(76,4)+0,5(50,1)+0,3(50,1)+0,3(197,6)} = 0,28$$

Pore solutions extractions made before and after a migration experiment tend to indicate that the latter assumption is reasonable [12].

The third migration coefficient was calculated according to an equation developed by Zhang and Gjorv [7, 13]. These authors derived a semi-empirical relationship between the chloride diffusion coefficient and the migration velocity of chloride ions on the basis the Einstein equation [13]:

$$D = 300\frac{kT}{ze_0E}V_d \tag{9}$$

where k is the Boltzmann constant, E the electrical field, e_0 charge of proton, and V_d the net velocity.

The relationship developed by Zhang and Gjorv [7, 13] is given in equation (10):

$$D_i = \beta\frac{T}{\psi}\frac{LV}{C_0A_0}\frac{dC_i}{dt} \tag{10}$$

where V the volume of solution, A_0 the surface area of the sample and dc/dt, the concentration gradient. In order to take into account the ionic interactions between the ionic drifts, the authors introduced an empirical correction factor β. This correction factor represents the ratio of the ideal to the actual drift velocity of ions. The actual drift velocity of ions is calculated considering the relaxation and electrophoretic effects of the ionic cloud around an ion described by the Debye-Hückel theory. Values of β for several sodium chloride (NaCl) concentrations (up to 0.5 mol/l) and several temperatures can be found in reference [7]. The value of β (1.48×10^{-4} JK^{-1} C^{-1}) used in this equation was that provided by the authors in reference [7].

Results and Discussion

The different diffusion coefficients (D_{F2}, D_{F1}, M, M_{cond}, and $M_{Z\&G}$) are summarized in Table 4. As can be seen, the values of the transport coefficient appear to vary significantly with the method considered. However, despite these variations, all coefficients appear to be sensitive to the same parameters. The transport coefficient was generally found to decrease with the water/binder ratio, the addition of silica fume and the addition of sand.

Figure 1 presents the evolution of the different transport coefficients as a function of the effective diffusion coefficient (D_{F1}). The choice of D_{F1} as a basis of comparison relies on the

TABLE 4

Diffusion and Migration Coefficients

Mixture	DF2 ($10^{-12}m^2/s$)	DF1 ($10^{-12}m^2/s$)	M ($10^{-12}m^2/s$)	Mcond ($10^{-12}m^2/s$)	MZ&G ($10^{-12}m^2/s$)
M25-0	1,6	0,8	0,1	1,2	0,3
M25-30	1,4	0,4	0,2	1,0	0,3
M25-50	1,2	0,5	0,1	0,6	0,2
M25(SF)-0	0,8	0,4	0,1	0,4	0,2
M25(SF)-30	0,1	0,5	0,1	0,6	0,2
M25(SF)-50	0,8	0,2	0,1	0,4	0,2
M45-0	16,7	9,5	4,5	11,0	6,4
M45-30	15,2	5,0	3,6	6,9	5,2
M45-50	14,4	4,0	2,7	4,8	4,3
M45(SF)-0	8,7	4,0	2,3	6,3	3,6
M45(SF)-30	6,3	2,0	0,8	2,0	1,3
M45(SF)-50	5,9	2,5	0,4	1,0	0,7
M45(50)-0	18,2	8,5	5,4	12,7	7,8
M45(50)-30	15,0	5,0	3,6	6,3	6,0
M45(50)-50	14,1	5,0	2,7	5,0	4,3

fact that it has been calculated by taking into account the interactions between the chloride ions and the hydrated cement paste. It should therefore be more accurate than the value of the apparent diffusion coefficient. As can be seen, there seems to be a good correlation between the different coefficients (D_{F2}, M, M_{cond}, $M_{Z\&G}$) and D_{F1}. The data presented in Figure 1 systematically show that:

$$D_{F2} > M_{cond} > D_{F1} > M_{Z\&G} > M$$

The difference between the transport coefficients calculated according to the different methods can be, in certain cases, very important. For example, the effective diffusion coeffi-

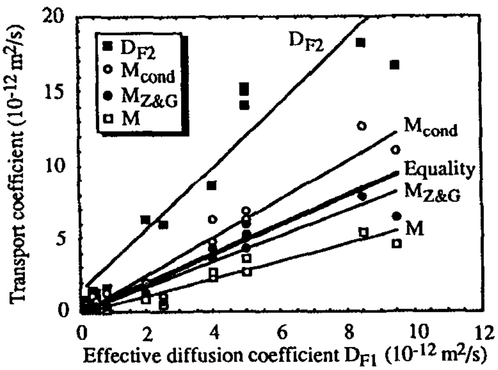

FIG. 1.

Relationship between the transport coefficient for the 15 mixtures and the effective diffusion coefficient (D_{F1}).

cients (D_{F1}) appear to be at least two times higher than the migration coefficients (M) while the apparent diffusion coefficients (D_{F2}) appear to be higher than the migration coefficients (M) by almost an order of magnitude.

These results seem to be in apparent contradiction with those reported by Tang [5] and Arsenault and Ollivier [13]. As previously mentioned, Tang [5] found a good correlation between the apparent diffusion coefficient D_{F2} (calculated from immersion tests) and the migration coefficient measured in an unsteady-state experiment. Arsenault and Ollivier [13] compared the diffusion coefficients obtained from steady-state diffusion and migration experiments. In their case, the effective diffusion coefficients were slightly higher than the migration coefficients. These results, however, clearly underline the complexity of determining the "true" diffusion coefficient.

As was previously mentioned, the total flow (J_i) of chloride ions passing through the sample and the correspondent current were recorded during the steady-state migration experiments. These values allow the calculation of the experimental transport number according to equation (6) which assumes that the contribution of the diffusing flow to the total flow remains limited. Each value (J_i and i) used in the calculations was determined when the steady-state regime has been reached. Table 5 presents the values of the experimental transport number for each of the mortar samples tested in this investigation.

As can be seen in Table 5, the experimental transport number (t_{exp}) is, at least, approximately 2 times lower than the theoretical transport number (t_{theo} = 0.28) which has been calculated assuming no interactions between the different diffusing flows. According to these results, it is not surprising that the conduction coefficients are systematically higher than the values of M since the determination of M_{cond} is based on the diffusion flux calcu-

TABLE 5

Experimental Transport Numbers

Mixture	Sample	t_{exp}	t_{the}/t_{exp}	Mixture	Sample	t_{exp}	t_{the}/t_{exp}
M25-0	1	0,04	7,00	M45(SF)-0	1	0,10	2,80
	2	0,04	7,00		2	0,10	2,80
M25-30	1	0,05	5,60	M45(SF)-30	1	0,10	2,80
	2	0,04	7,00		2	0,10	2,80
M25-50	1	0,05	5,60	M45(SF)-50	1	0,13	2,15
	2	0,05	5,60		2	0,10	2,80
M25(SF)-0	1	0,08	3,50	M45(50)-0	1	0,12	2,33
	2	-	-		2	0,12	2,33
M25(SF)-30	1	0,16	1,75	M45(50)-30	1	0,16	1,75
	2	0,13	2,15		2	0,14	2,00
M25(SF)-50	1	0,09	3,11	M45(50)-50	1	0,17	1,65
	2	0,07	4,00		2	0,14	2,00
M45-0	1	0,11	2,55				
	2	0,11	2,55				
M45-30	1	0,16	1,75				
	2	0,13	2,15				
M45-50	1	0,18	1,56				
	2	0,15	1,87				

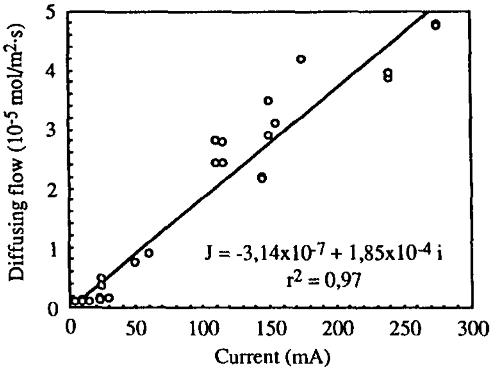

FIG. 2.
Relationship between the experimental flux of chloride ions and the total current.

lated with the theoretical transport number which has been found to be higher than the experimental transport number. The fact that the theoretical transport number is higher than the experimental transport numbers indicate that the hypothesis of independent diffusing flows (for the electrolytes used in the present investigation) is clearly not valid. In this respect, equation 4 cannot be used to accurately determine the chloride ion diffusion coefficient since this equation was developed on the basis of a negligible electrical coupling of the diffusing flows.

The results given in Table 5 also indicate that the difference between the experimental and theoretical transport numbers increases with a reduction of the water/binder ratio and, for the 0.45 water/binder ratio series of mixtures, with the addition of silica fume. For example, the experimental transport number in approximately 5 to 7 times lower than the theoretical transport number for the M25 series of mixtures while it is approximately 2 times lower for the M45 mixtures. This tend to indicate that the fraction of current transported by chloride ions may be dependent upon the microstructure of the cementitious system. Such a phenomenon can probably be attributed, at least in part, to the electrical double layer effect. As suggested by Chatterji [14], the presence of over-lapping double layers should have a significant influence of the ion transport mechanisms in cement-based materials, especially for low water/binder ratio systems.

As pointed out by Andrade [10], experimentation would be easier to carry out if one has only to measure the total current instead of the total flow of chloride ions passing through a concrete sample. Figure 2 presents the total flow of chloride ions (J_i) passing through the mortar samples in the migration experiments as a function of the total current (i). As can be seen, these experimental parameters appear to correlate quite well, the correlation factor being more than 97%. However, this relationship is probably valid only for the experimental set up and the electrolytes used in the present investigation. The good correlation between these two parameters opens a door for a simplified experimental determination of the diffusion coefficient. However, as it has been previously emphasized, there exists actually no models that permits the calculation of reliable diffusion coefficient on the basis of current data.

Conclusion

The results presented in this paper indicate that the values of the transport coefficient appear to be dependent upon the test method used to measure and calculate that coefficient. Even if the discrepancy between the different methods can be, in certain cases very important, it appears that all these methods are quite sensitive to the material microstructure and can thus probably be used to qualitatively assess the ability of a cementitious system to resist the chloride ion ingress.

All these transport coefficients were calculated using several simplifying assumptions, the most important being probably that there were no interactions between the diffusion flow of each ionic species. According to the experimental results presented in this paper, the assumption of the independence of the various ionic flows is clearly not valid. Moreover, the interdependency of ionic flows appears to be a function of the material microstructure. The interactions were found to increase with a reduction of the water/binder ratio and the use of silica fume.

The good correlation between the total flow of chloride ions and the total current opens a door to a simplified experimental test procedure that could be used to determine the chloride ion diffusion coefficient. However, more research is clearly needed before a "true" diffusion coefficient can be determined from such an experimental procedure.

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