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A novel method for describing chloride ion transport due to an electrical gradient in concrete: Part 2. Experimental study

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Abstract

This paper is the second of a set of two that develops a novel method for describing the transport of chloride ions in concrete under an electrical gradient. In Part 1, the development of a method to predict the movement of chloride ions under an electrical gradient is outlined. This new theory is designed to correct some deficiencies of the current state of the art. Namely, it considers the effect of concrete being a porous media rather than considering concrete as an aqueous solution as is done with the standard laws, e.g., the Nernst–Planck equation. In this part, experimental evidence is presented to support the theory.

Keywords: Concrete; Transport properties; Pore size distribution; Ionic migration

1. Introduction

Understanding the movement of chloride ions through concrete is of importance to both service life modeling and correct interpretation of test results. In Part 1 of this series [1], a novel method for describing the movement of ions due to an electrical potential gradient was described. In this paper, experimental evidence is presented to support the new method. This evidence is based on a series of profiles of concrete samples tested in both the rapid migration test (RMT) [2,3] and from steady-state migration cells [4].

2. Theory

In a companion paper, a theory has been developed to describe the movement of chloride ions in concrete under an electrical potential gradient [1]. This theory was developed considering the influence the matrix has on the movement of chloride ions and that the chloride ions are not simply moving through a uniform solution. The presence of the concrete matrix contributes an additional modification to the penetrability of the concrete. The magnitude of this modification will vary from location to location, depending on the specific properties of the pore structure at any point. The modifications to penetrability will be lognormally distributed. The equation describing the chloride concentration profile for a constant surface concentration then becomes:

$$C = C_0[1 - F(y, \lambda, \zeta)] + C_i \tag{1}$$

where C_0 is the surface chloride concentration, C_i is the initial background chloride concentration and ζ and λ are parameters representing the variation and the average modification to penetrability,

$$y = \frac{x}{\left(\frac{zFUDt}{RTL}\right)} \tag{1a}$$

where x is the depth of the point of interest, z is the ionic valence, F is Faraday's constant, U is the electrical potential, D is the diffusion coefficient of the ion in free solution, t is the duration of the test, R is the gas constant, T

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is the temperature, L is the length of the specimen and $F(y,\lambda,\zeta)$ is

$$F(y,\lambda,\zeta) = 1 - \int_0^y \left(\frac{1}{\sqrt{2\pi(\ln(\zeta))^2 \ln(u)}} \times \exp\left[-\frac{1}{2}\left(\frac{\ln(u)-\ln(\lambda)}{\ln(\zeta)}\right)^2 \right] \right) \mathrm{d}u \qquad (1b)$$

In addition, the surface concentration can be calculated as the product of the available porosity and the solution concentration. This results in two material parameters describing the movement of chloride ions (λ and ζ). The surface concentration, C_0, can be calculated as the product of the porosity and the solution concentration. The porosity used was that available when the samples were conditioned to 11% RH. At this moisture condition, a monolayer of water molecules will line the pore walls [5], which will not participate in transport. The calculated surface concentration is the free surface concentration and does not include the contribution of the background chloride values. It also does not consider the quantity of bound chloride ions, which cannot be predicted a priori.

3. Experimental procedures

To evaluate the proposed model, a series of test was conducted on a set of six different concretes of various qualities and compositions. The mixture proportions used are outlined in Table 1. At test, the concretes ranged in age from 12 to 18 months and had been continuously stored at 23 °C at >95% RH. The specimens were 50-mm-thick slices cut from 100-mm diameter cylinders.

3.1. RMT procedure

To examine the transport properties of the concretes, it was necessary to perform a series of transport experiments. A series of tests based on the RMT were done. The test procedure has been described previously [2,3] and is only briefly described herein. To perform the RMT, a saturated 100-mm diameter, 50-mm long concrete sample is placed in a sleeve and then set in the test apparatus as shown in Fig. 1. On one side of the sample, the solution contains chloride ions, while the other is chloride free. An electrical potential is then applied such that the chloride ions are driven into the concrete for given time. In this work, the applied voltages and durations were varied to fully investigate this phenomenon. Five different combinations of voltage and test duration were used. For all the concrete, except the one containing corrosion inhibitor, these combinations were 60 V for 18 h, 60 V for 9 h, 60 V for 6 h, 30 V for 36 h and 10 V for 108 h. Sixty volts for 18 h was used to match the standard test procedure. In addition, to explore how the profiles develop over time, the two shorter durations were used at the same voltage. To determine if the magnitude of the external impetus had an influence, the two lesser voltages were used. So that these samples had the same distance traveled, their durations were extended so that the product of their voltage and durations remained a constant. The concrete containing corrosion inhibitor could not be tested using a voltage of 60 V. The increased conductivity of the pore solution caused the current experienced to be too great for the power supplies. Thus, the conditions used were 30 V for 36 h, 30 V for 18 h, 30 V for 9 h, 20 V for 54 h and 10 V for 108 h. Two replicates were done for each test condition.

After the specimens were subjected to this voltage, their chloride profiles were then established. This consists of removing small (~0.5–0.75 mm thick) layers of concrete by dry grinding with a mill mounted so that the axis of advance is parallel to the direction of transport during the test. The powder thus created is then digested in nitric acid to extract the chloride ions. The solution so created is then tested for chloride concentration using potentiometric titration and this is then related to the chloride concentration in the concrete. The profile was determined to the depth at which the chloride concentration approximately reaches the background level, as previously established on a piece of concrete never exposed to chloride ions, if it was possible. For some samples, the chlorides penetrated deeper than the mill could penetrate.

Table 1
Concrete mix designs

	0.45, Plain	0.35, Plain	0.45, SF	0.40, FA	0.45, SF, FA	0.45, DCI
w/cm	0.45	0.35	0.45	0.40	0.45	0.45
Cement (kg/m^3)	362.5	418.0	333.5	300	266.8	362.5
Fly ash (kg/m^3)	0	0	0	75.0 (20%)	72.5 (20%)	0
Silica fume (kg/m^3)	0	0	29.0 (8%)	0	23.2 (6.4%)	0
Water (kg/m^3)	163.0	146.0	163.0	150.0	163.0	163.0
Coarse aggregate (kg/m^3)	1025	1025	1025	1025	1025	1025
Fine aggregate (kg/m^3)	698	695	681	700	668.2	698
Corrosion inhibitor (l/m^3)	0	0	0	0	0	30

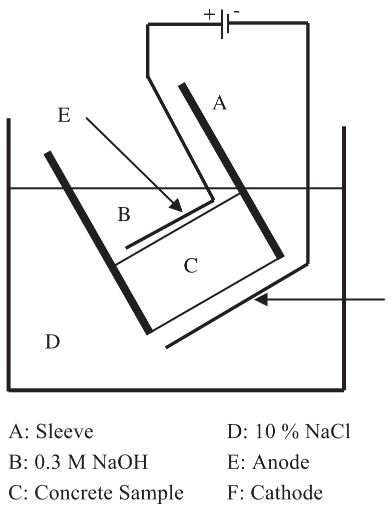

Fig. 1. RMT set-up.

In these cases, chloride profiles were determined to this maximum depth ($\sim$40 mm). As not all samples could be profiled immediately, they were stored in a freezer at a temperature below −10 °C until they could be profiled to prevent additional transport during storage. No samples were stored longer than 28 days and most for considerably shorter than that. In addition, two replicate samples, one profiled immediately and one not profiled until after a 4-week storage period, did not have profiles that were any more different than any other two replicates.

3.2. Steady-state migration test procedure

In addition to the RMT, another test was performed to further examine the transport of ions in the concrete. A steady-state migration test was performed on two samples for each concrete. This test is similar to the RMT in that chloride ions are driven into a concrete sample by an electrical potential. Instead of the chloride penetrating only partway through the sample, however, the test is continued until the chloride ions penetrate through the entire sample to the solution on the other side. This downstream solution is then monitored for chloride ion concentration. Fig. 2 is a diagram of the steady-state migration apparatus. A more complete description of the steady-state migration test is provided by McGrath and Hooton [4].

In this case, the test conditions were selected to match the RMT. An upstream concentration of 10% NaCl and a downstream concentration of 0.5 M NaOH was used. Except for the corrosion inhibitor-containing concrete, 60 V were used on one of the samples. The other was subjected to either 30 V (0.45, SF; 0.40, FA; 0.45, SF, FA) or 10 V (0.45, Plain; 0.35, Plain) depending on their expected penetrability. The samples containing corrosion inhibitor were subjected to both 30 and 10 V.

4. RMT profile fitting and establishment of material parameters

The experimental profiles were then fit to Eq. (1) and the dimensionless material parameters (the mean penetrability, λ, and the variation of that penetrability, ζ) were determined. A least squares regression procedure was adopted. The two parameters were consecutively altered such that the pair of values that resulted in the least value for the sum of the squares of the errors was determined. These results are reported in Table 2 for all of the profiles. In addition, the determined correlation coefficients (r^2) are reported. As can be seen, the r^2 values are all high, typically above .90, with most values being substantially higher. One set of curves was not fit as satisfactorily, however. This was for the concrete containing corrosion inhibitor. An examination of Table 2 reveals significantly lower correlation coefficients for some of these profiles. This is attributed to the greater conductivity of the pore solution caused by the presence of nitrite ions. The Nernst–Planck equation used to calculate the distance the ions would travel in solution and thus to normalize the distance is a simplification of the situation that occurs in solutions. It neglects the effect of other ions. This effect would obviously be more significant when there are ions present with a greater mobility. It is believed that this could be overcome by using a more complicated model to predict the distance traveled in solution. However, this would come at the expense of more complicated equations as well as requiring more information about entire state of the concrete, e.g., the distribution of the other ions present. Due to this, the concrete containing corrosion inhibitor will be neglected in further discussion.

To aid in the examination of the determined transport parameters, Fig. 3 was constructed. It contains the mean penetrability on the x-axis and the dispersion on the y-axis. Plotted are the established parameter pairs from the 10 RMT profiles of each concrete. In addition, an oval has been drawn about the sets of pairs of each concrete, indicating the region where the relevant transport parameters lay. An examination of this diagram indicates that, while there is some scatter in the results, the results for each concrete do lie in a discrete area. This indicates that the parameters are a function of the concrete itself and not the test results. Thus, the results from a transport test can be used to characterize a concrete and are a description of the transport properties of that concrete.

One test characteristic that may have an influence on the determined parameters would be the distance the furthest ion has traveled. In a single concrete, if the ions are traveling farther, they have in effect passed through more of the different pore segments. This may be expected to have the effect of reducing the spread in the results—if an ion passes through a greater portion of the pore structure, it becomes less likely that the ion will experience an extreme value of penetrability for its entire distance, causing the average rate of travel of that ion to become closer to the

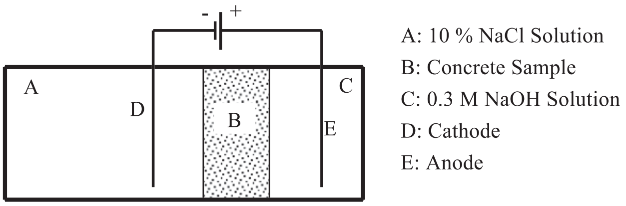

Fig. 2. Migration cell set-up.

mean. Because different test conditions were used to establish the profiles, it was possible to test if this may have had an influence on the parameters. In these cases, the product of the voltage and the test duration was used as a measure of the relative distance the ions are traveling within a single concrete. Figs. 4 and 5 were constructed comparing that parameter with both the mean (λ) and the deviation (ζ). Within a single concrete, no trend is apparent in the mean value or in the deviation with depth of penetration (the product of voltage and duration). Thus, the distance the ions travel, at least within this range, does not influence the test results.

5. Steady-state migration predictions

The traditional method has been to use the unmodified Nernst–Planck equation to evaluate these results. As previously discussed, this is believed to be incorrect. The equations previously described accounting for the influence of the pore structure will be used to fit the curves and establish transport parameters. These will be compared with the parameters determined from the RMT profiles.

To predict the chloride mass passed with time, the forward finite difference approach was used. The increase in the mass of chloride in the downstream cell is due to the chloride ions that have passed out of the concrete. At a

Table 2
RMT fitted transport parameters

	Test conditions (voltage/duration)	Sample 1			Sample 2		
		Mean (λ) ($\times 10^{-4}$)	Deviation (ζ)	r^2	Mean (λ) ($\times 10^{-4}$)	Deviation (ζ)	r^2
0.45, Plain	60/18	10.9	7.10	.9428	27.0	3.53	.9574
	30/36	21.2	2.80	.9813	17.0	4.77	.9061
	10/108	8.59	4.41	.9758	14.7	2.81	.9759
	60/9	34.2	2.18	.9719	10.4	4.18	.9766
	60/6	15.4	3.40	.9502	23.1	3.10	.9461
	Average	λ	1.82×10^{-3}		ζ	3.83	
0.35, Plain	60/18	18.7	1.65	.9620	13.9	1.89	.9485
	30/36	15.6	1.59	.9363	7.70	2.35	.9327
	10/108	10.1	1.81	.9807	8.51	2.18	.9281
	60/9	15.2	1.87	.9661	16.6	1.98	.9421
	60/6	12.0	1.95	.9714	16.1	1.92	.9517
	Average	λ	1.34×10^{-3}		ζ	1.92	
0.45, SF	60/18	6.41	2.70	.9642	6.83	2.44	.9907
	30/36	3.09	4.04	.9832	4.47	3.73	.9820
	10/108	4.99	2.60	.9926	4.19	3.16	.9859
	60/9	3.59	4.18	.9766	4.24	3.50	.9933
	60/6	3.34	3.72	.9818	3.40	4.67	.9511
	Average	λ	4.46×10^{-4}		ζ	3.47	
0.40, FA	60/18	4.68	2.03	.9958	3.08	3.19	.9844
	30/36	3.74	2.89	.9943	2.21	3.80	.9826
	10/108	3.13	2.80	.9961	4.93	2.34	.9797
	60/9	6.05	2.25	.9957	4.87	2.12	.9989
	60/6	3.73	3.08	.9305	4.87	2.60	.9823
	Average	λ	4.13×10^{-4}		ζ	2.71	
0.45, DCI	30/18	30.7	2.27	.9283	36.7	2.24	.8421
	20/54	45.8	11.57	.7183	35.7	13.00	.6982
	10/108	26.3	2.14	.9580	29.5	1.99	.9521
	30/36	42.0	2.23	.9260	37.3	3.12	.9760
	30/9	27.3	2.41	.9081	32.1	2.44	.9667
	Average	λ	3.43×10^{-3}		ζ	4.34	
0.45, SF, FA	60/18	1.32	3.46	.9920	1.22	2.44	.9860
	30/36	1.45	2.98	.9700	1.25	2.99	.9599
	10/108	1.60	2.13	.9730	1.26	3.46	.9567
	60/9	2.49	2.57	.9967	0.962	5.05	.9787
	60/6	2.58	2.24	.9732	0.895	4.39	.9132
	Average	λ	1.50×10^{-4}		ζ	3.17	
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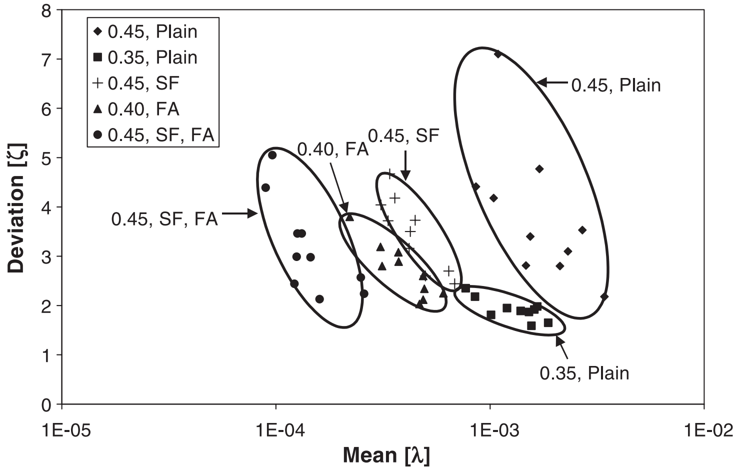

Fig. 3. RMT parameter evaluation.

given time step, the concentration at the downstream surface (corresponding to a depth equal to the specimen thickness) was calculated from Eq. (1). In addition, the distance the chloride ions that were at the end surface at the last time step traveled was also calculated from the ratio of the two times multiplied by the specimen length. The mass of chloride in the region that had passed out since the last time step was determined as the product of the concentration at the end surface, the distance the ions traveled, the area of the specimen and the density of concrete. The density is necessary as the concentration is expressed on a mass basis. The cumulative mass passed was then determined as the running total. Numerically, this can be expressed as:

$$m_i = m_{i-1} + \Delta m_i \tag{2}$$

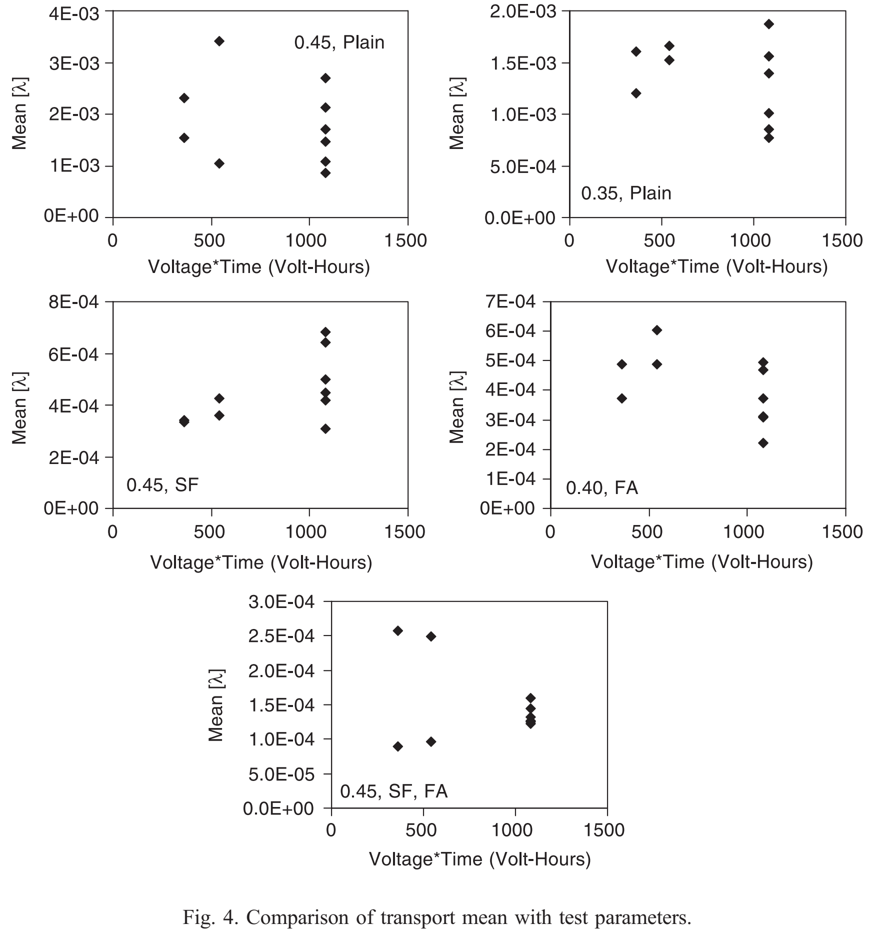

Fig. 4. Comparison of transport mean with test parameters.

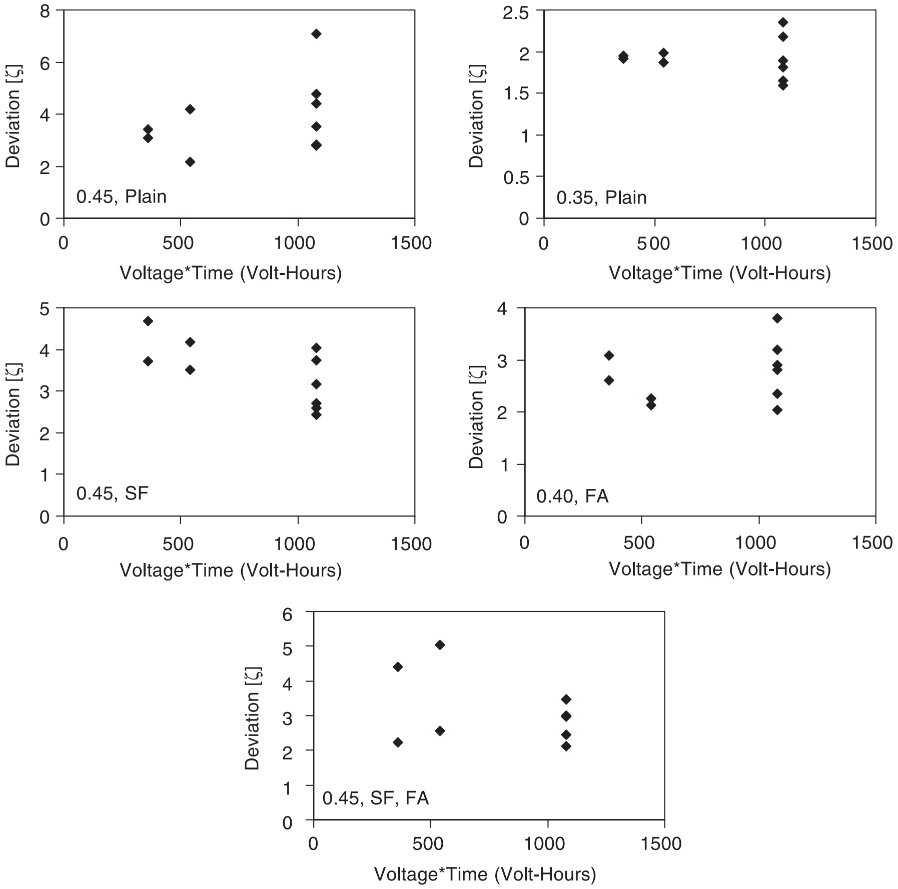

Fig. 5. Comparison of transport deviation with test parameters.

where m_i is the cumulative mass passed at time i and Δm_i is the incremental mass passed from time i and time $i-1$, calculated from:

$$\Delta m_i = C_i\left(\frac{t_i}{t_{i-1}} - 1\right)LA\rho \qquad (3)$$

where C_i is the concentration at the downstream face at time i calculated from Eq. (1), t_i is time i, L is the length of the specimen, A is the cross-sectional area of the specimen and ρ is the density of concrete. The time is zero when the voltage is initially applied.

For the steady-state migration cells, it was possible to fit the cumulative mass passed as a function of time curves very successfully. The resulting parameters are shown in Table 3. For this test, it was possible to successfully fit the results of the corrosion inhibitor-containing concrete as well. For this test procedure, the fits were generally more successful than for the RMT, with correlation coefficients above .98 and normally above .99.

To compare the transport parameters determined from steady-state migration with the transport parameters from the RMT, Fig. 6 was constructed. It is a repeat of Fig. 3, with the addition of the parameters from the steady-state migration tests as open symbols. It can be seen that the parameters from the steady-state migration experiments lie outside the region of the parameters from the RMT. In general, the deviation is less and the mean value is greater when determined from the steady-state migration experiments. This is attributable to the different binding characteristics of the two tests. As previously discussed, for the RMT, the binding is ongoing during the entire testing period. For the steady-state migration test, however, all the binding can be assumed to occur during the initial period when the

Table 3
Migration fitted parameters

Concrete	Test voltage (V)	Mean (λ) ($\times 10^{-4}$)	Deviation (ζ)	r^2
0.45, Plain	60	52.1	1.10	.9936
0.45, Plain	10	29.9	1.29	.9965
0.35, Plain	60	26.4	1.15	.9954
0.35, Plain	10	12.5	1.22	.9949
0.45, SF	60	11.4	1.18	.9952
0.45, SF	30	10.4	1.20	.9988
0.40, FA	60	11.3	1.13	.9794
0.40, FA	30	10.0	1.17	.9889
0.45, DCI	30	68.8	1.22	.9984
0.45, DCI	10	51.0	1.30	.9912
0.45, SF, FA	60	4.90	1.24	.9944
0.45, SF, FA	30	4.93	1.55	.9932

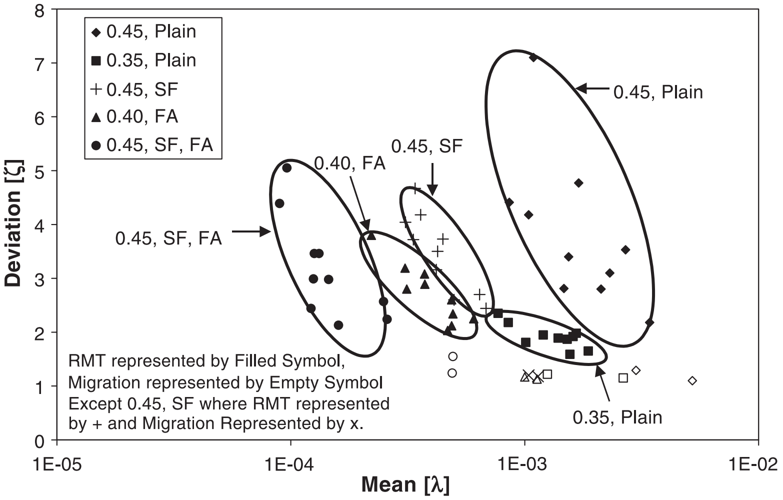

Fig. 6. RMT parameter evaluation including results of migration cells.

chloride ions are traveling through the concrete and not during the steady-state buildup phase. It is the phase after the chlorides have passed through the concrete that dominates the behavior for the steady-state migration test and thus controls the value of the parameters that would be fit. It is intuitive that the effect of binding would be to slow the average rate of transport of the chloride ions (decreased mean for RMT) and to cause the ions to spread out (increase deviation).

6. Conclusions

Two types of tests were performed to test the theory developed to predict the migration of chloride ions in concrete. The principal test was the RMT where a voltage is applied for a given time and the chloride profile in the concrete is determined. In addition, steady-state migration tests were conducted where the mass of chloride ions passing through a concrete is monitored with time. The results from both test procedures could be fitted to the equations developed in Part 1.

The fitted material parameters were found not to be a function of the test conditions of the RMT. Thus, the fitted parameters are material parameters and not affected by the test conditions. However, the parameters determined from the steady-state migration cells were different from that determined from the RMT. The mean penetrability value was slightly higher and the variation in penetrability was much higher. This was attributed to the difference in binding situation. For the RMT, binding is occurring during the measured transport. For the steady-state migration test, the binding has mostly occurred during the initial portion of the test and is no longer occurring during the time when the chloride is building up in the downstream cell.

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