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The Effect of Other Ions on Chloride Migration in Concrete.

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ABSTRACT

Measuring chloride migration is essential for predicting the durability of embedded steel in concrete. The "Rapid Chloride Permeability Test" to ASTM C1202 is gaining popularity as a method for this but it has severe limitations, particularly when pozzolanic admixtures are used. The NTBuild-492 Migration test overcomes some of these but still does not take full account of the complex processes involved. This paper will provide an explanation of these problems which is based on multi-species modelling. An overview of a major experimental programme to test and validate the models will be presented. The programme concluded that even in diffusion tests in which there is no electric field applied or electrical measurements made, there are still significant effects of charge build up from hydroxyl, sodium and potassium ions as well as the chloride.

1. INTRODUCTION

The purpose of this paper is to discuss the concept of the diffusion coefficient for migrating species in concrete. The problems with measuring this parameter are illustrated by discussing some of the measurement techniques and the application of the results when they are obtained (Lizarazo-Marriaga 2009).

The three tests that will be discussed are the "Rapid Chloride Permeability Test" to ASTM C1202, the Nordtest NTBuild-492 test and a simple diffusion test with no applied voltage. The applications that will be considered are the comparison of different mixes and also the calculation of the working life of structures using models such as life-365.

Before considering these situations the basic definitions are presented.

2. DEFINITIONS OF DIFFUSION COEFFICIENTS.

2.1 Diffusion in a homogeneous non-adsorbing system.

Diffusion is driven by concentration gradient and is defined in equation 1 (Fick's law) (Crank 1976):

$$F = D \frac{dC}{dx} \quad \text{kg/m}^2/\text{s} \quad (1)$$

where:

F is the flux in $\text{kg/m}^2/\text{s}$

D is the diffusion coefficient in m^2/s

C is the concentration in kg/m^3

x is the position.

2.2 Adsorption in a porous solid

Adsorption is considered in this paper because it is important to show that the conclusions will apply equally to an adsorbing or a non-adsorbing system.

The concentration of ions in a porous solid may be measured in two different ways (Atkinson and Nickerson 1984):

C_l kg/m^3 is the concentration of ions per unit volume of liquid in the pores
and

C_s kg/m^3 is the total concentration (including adsorbed ions) per unit volume of the solid.

2.3 Diffusion with adsorption.

Because there are two different ways of measuring concentration in an adsorbing system there are also two different ways of measuring diffusion:

The apparent diffusion coefficient D_a is defined from:

$$F = D_a \frac{dC_s}{dx} \quad \text{kg/m}^2/\text{s}$$

and the intrinsic diffusion coefficient (which is the diffusion coefficient for the pore solution) is defined from:

$$F' = D_i \frac{dC_l}{dx} \quad \text{kg/m}^2/\text{s}$$

where F' is the flux per unit cross sectional area of the liquid in the pores. Thus:

$$F = \varepsilon D_i \frac{dC_i}{dx} \quad \text{kg/m}^2/\text{s}$$

where ε is the porosity

2.4 Electromigration

If an electric field is applied across the solid the negative ions will move towards the positive electrode. Classical theory of electrochemistry defines the flux due to electromigration using the same diffusion coefficient as used in Fick's law in equation (2):

$$J = \frac{DzECF}{RT} \quad (2)$$

where

J is the flux in kg/m²/s

z is the valency of the ion

F is the Faraday constant

E is the electric field in volts/m

R = gas constant

T is the temperature in °K

Rearranging this gives the Nernst-Einstein equation:

$$D_i = \frac{RT\sigma_i}{z_i^2 F^2 c_i}$$

Where σ is the electrical conductivity

2.5 Combining Diffusion and Electromigration.

The general law governing the ionic movements due to the chemical and electrical potential is obtained by combining equations (1) and (2) and known as the Nernst-Planck equation:

$$J_i = D_i \frac{\partial c_i}{\partial x} + \frac{z_i F}{RT} D_i c_i \frac{\partial V}{\partial x}$$

Where V = Voltage, thus $\delta V/\delta x$ = Electric field (Crank 1976)

3. TESTS FOR DIFFUSION

3.1 Applying the theory of diffusion to the ASTM C1202 Test

3.1.1 The test method (ASTM 2005)

The ASTM C1202 test is shown schematically in figure 1. In this test sodium chloride is added to one cell and sodium hydroxide to the other and a voltage is applied across the sample. In order to calculate what happens next it is necessary to consider the physical situation in the sample. Charged ions can only move if charge neutrality is preserved. Thus, for example, a negative chloride

ion can only move to a region of the sample if either its sodium counter-ion moves with it or a different negative ion such as a hydroxyl ion is displaced ahead of it. If charge neutrality is not preserved electric fields build up to prevent the movement. Thus the ability of the chloride ion to move through the region the region of the sample is determined by the concentration and mobility of other ions in the region. Referring to the Nernst-Einstein equation this may be represented as a change in conductivity (or resistivity) of the region. One effect of this is shown in figure 2. The different resistivities in different regions of the sample make the voltage drop across it non-linear. The difference between the measured voltages and the linear change is known as the membrane potential.

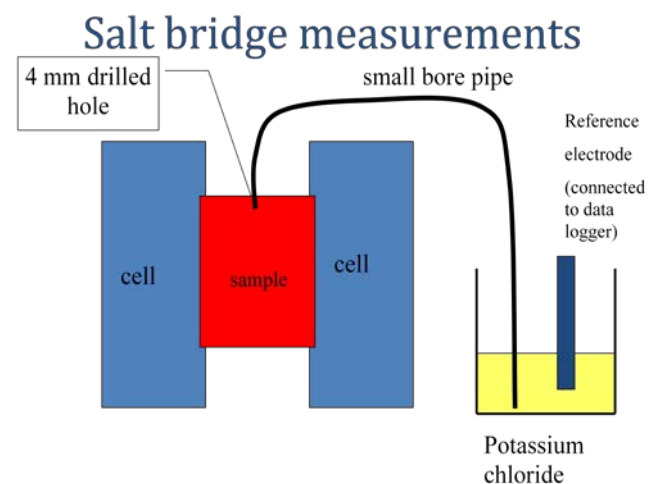


Figure 1. The ASTM C1202 test

Section through sample during test

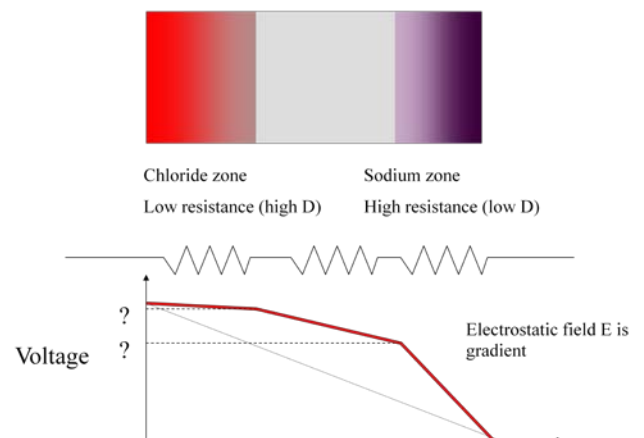


Figure 2. Schematic diagram of the effect of changes in resistivity

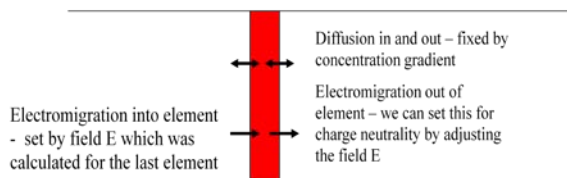
3.1.2 Modelling the diffusion (Lizarao-Marriaga and Claisse 2009 a,b)

The Nernst-Planck equation can be integrated to give changes of concentration and current with time, but this takes no account of the effect of other

ions. In order to do this it is necessary to use a numerical model. The model which is discussed in this paper uses repeated applications of equations (1) and (2) throughout space and time. However in order to apply equation (2) it is necessary to know the electric fields and, as shown in figure 2. This changes and is extremely difficult to calculate. The model therefore avoids this calculation by applying Kirchoff's law which states that the current must be the same at all points through the sample, i.e. charge neutrality must be maintained. In the computer code the net charge is calculated for different values of electric field on an iterative basis until the correct value is obtained to achieve neutrality. This process is shown schematically in figure 3.

Modelling a thin slice of the sample for a short time step

Apply Kirchoff's law : current in = current out



Final adjustments are needed to get the correct total voltage across the sample.

Figure 3. The basis of the model.

The model can be used to get diffusion coefficients from experimental results from the test by using Artificial Neural Networks which have been trained on repeated runs of the model with different coefficients and capacity factors for the different ions.

3.1.3 Results for the ASTM C1202 tests

Before considering results, the model was validated. This was achieved by measuring the mid-point voltage in test sample (as shown in figure 1). Experimental results for this are shown in figure 4 and these were shown to agree with the model.

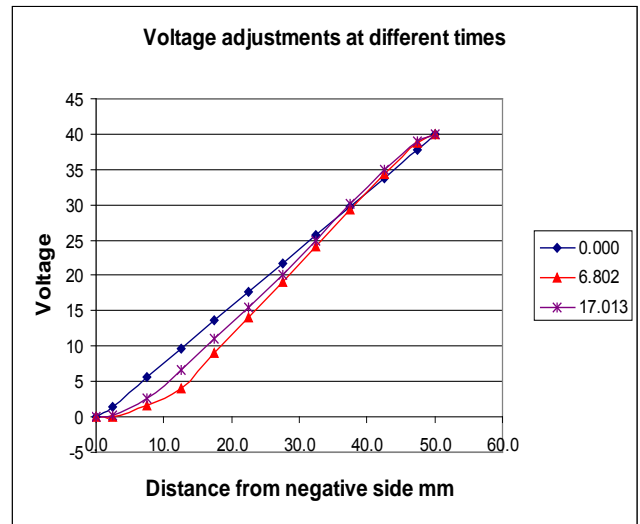


Figure 4. Mid-point voltages

The main result that is obtained from this test is the total charge passing. This is taken as a measure of the diffusion coefficient of the sample. Figures 5 and 6 show modelled current for a given sample (the area under the curve is the charge). Figure 5 shows the result for the full model and figure 6 shows the same result without the voltage control algorithm used to achieve charge neutrality.

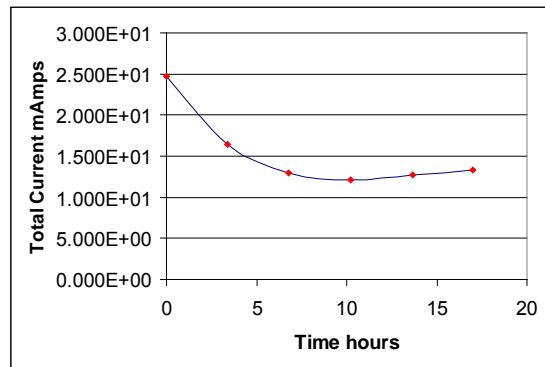


Figure 5. Current vs. time with voltage control

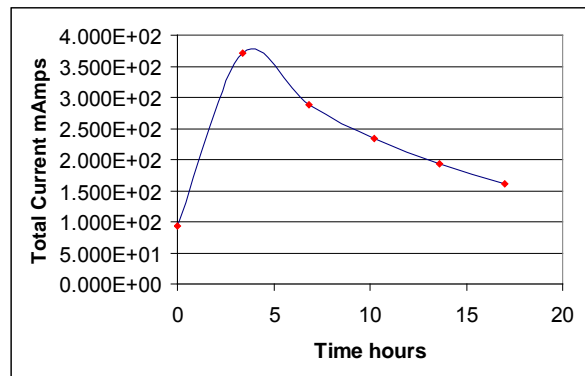


Figure 6 Current vs time without effect of other ions

It may be seen that the requirement for charge neutrality (i.e. the effect of the other ions) is very significant.

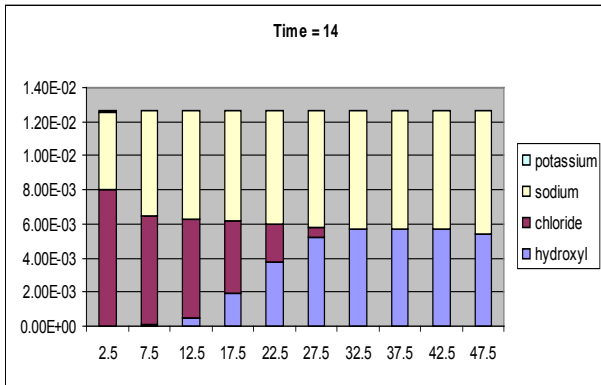


Figure 7. Showing the current carried by the different ions in Amps vs. the distance from the cathode side in mm 14 hours after the start of a test.

Figure 7 shows how the current during the test is carried by a number of different ions. The charge neutrality requirement makes the total current the same at each location.

3.2 The Nordtest NT Build-492 Test (Nordtest 1999)

This test is shown in Figure 8 is similar to the ASTM C1202 test in that a voltage is used to drive chlorides into the sample. However the results are obtained by cutting up the sample and measuring the chloride content at different depths at the end of the test. The results are then analysed using an integrated form of the Nernst-Plank equation. No account is taken of the ion-ion interactions.

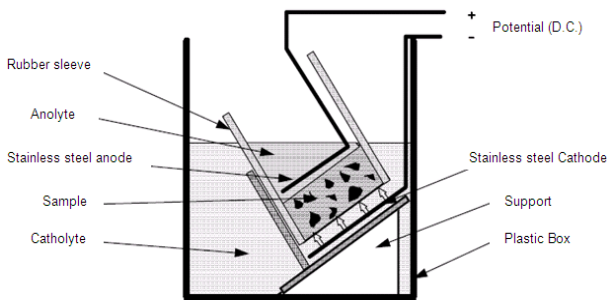


Figure 8 Arrangement of the migration test (NTBuild-492)

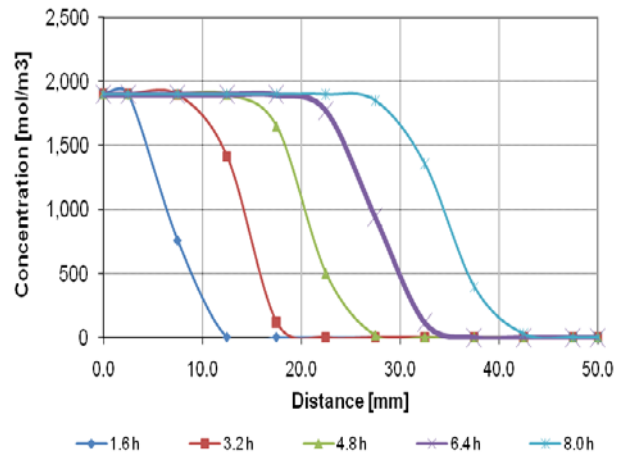


Figure 9. Modelled results for the NTBuild-492 test using the Nernst-Plank equation

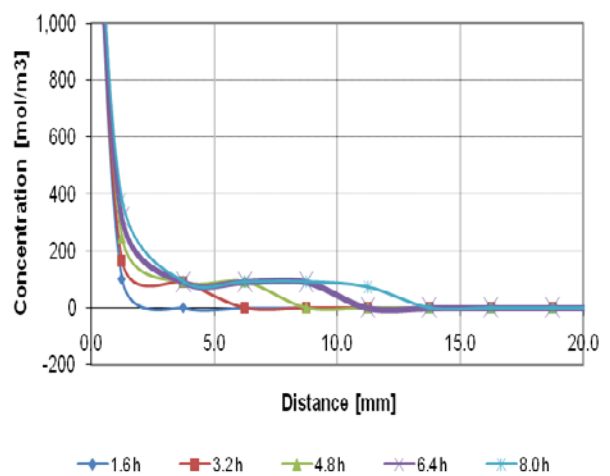


Figure 10. Modelled results for the NTBuilds-492 test with ion-ion interactions.

Figures 9 and 10 show the effect of ion-ion interactions on this test. They may be seen to be very significant

3.3 A Simple Diffusion Test

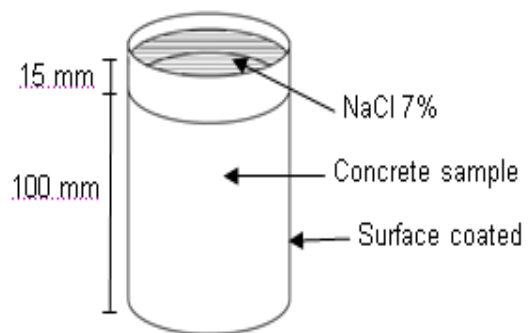


Figure 11. Simple diffusion test

Figure 11 shows a simple diffusion test. Despite the fact that there is no applied voltage there are still electric fields present as soon as ions start to

diffuse. The modelling of the test is different from the electrical tests because the boundary condition is one of zero current rather than a fixed voltage. Indeed a voltage can be measured across the sample during a test – it works as a type of simple battery. Figure 12 shows modelling and experimental results from a test.

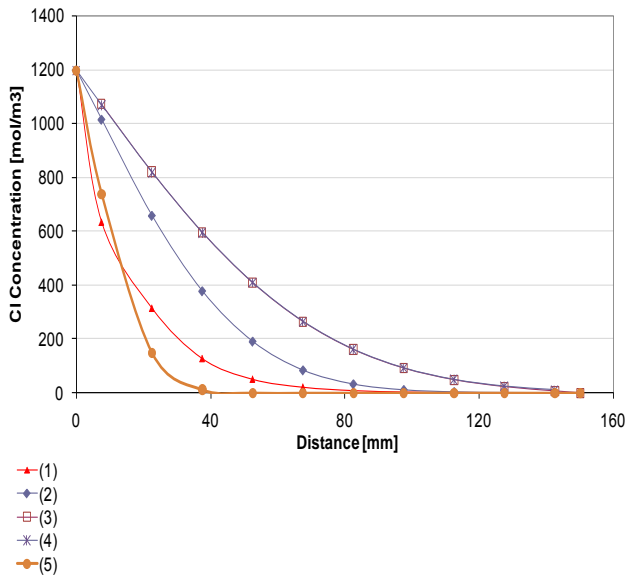


Figure 12. Results of simple diffusion test. (1) is the full model with zero current (2) is the model with current permitted (i.e. simulating what would happen if the ends of the sample were electrically connected) (3) and (4) show the computer model with the ion-ion interactions switched off and the result from integrating Fick's law. These gives the same results so the lines coincide – validating the computer model. (5) Is based on experimental data

From figure 12 it may be seen that obtaining values for diffusion coefficients from this type of experiment by simply integrating Ficks's law will give misleading results.

4. APPLICATIONS FOR THE DIFFUSION COEFFICIENT

4.1 Comparing different mixes (Lizarazo-Marriaga and Claisse 2010)

It is common practice to use the ASTM C1202 test to compare different mixes when publishing research on potential new cementitious components for concrete.

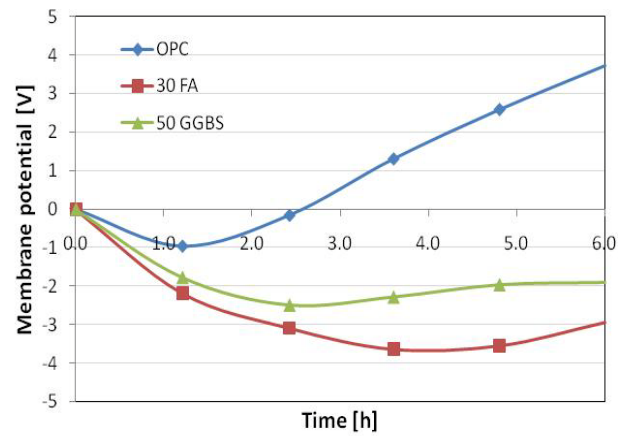


Figure 13. The membrane potential (i.e. the difference between the voltage and the linear voltage drop) for mid-point voltages in an ASTM C1202 test for OPC (CEM1), 30% PFA (Pulverised fuel ash) and 50% GGBS (Ground Granulated Blastfurnace Slag)

From Figure 13 it may be seen that changing the cementitious components in a mix has a significant effect on ionic voltages. This is because they significantly change the ionic concentrations (e.g. pozzolans deplete hydroxyl ions).

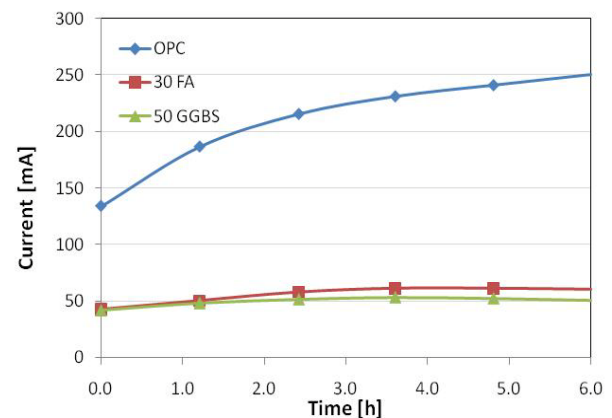


Figure 14. Showing current vs. time data for the GGBS and PFA mixes shown in figure 13.

From figure 14 it may be seen that the total charge passing is very different for the different mixes. This difference is caused by ion-ion interactions and does not indicate a change in the diffusion coefficient.

4.2 Modelling Concrete Durability

Software packages such as Life-365 (NRMCA 2011) us an integrated version of Fick's law and take no account of ion-ion interactions. These packages are used to predict the life of structures and influence design decisions such as the depth of cover to the reinforcement of the water/cement ration of the mix.

The package is set up so recommended values of the diffusion coefficient are given for different

mixes however it would be possible for users to input their own values if experimental data was available.

5. DISCUSSION

From the initial definitions of the diffusion coefficient it may be seen that there are two values, the apparent and the intrinsic. To see the difference, a simple diffusion test is considered in which chloride migrates into a sample and the concentration is then obtained at various depths. If the concentration is measured by sampling the pore solution the intrinsic coefficient will be measured but if the total concentration is obtained by acid dissolution of the solid this will give the apparent coefficient. The difference between them is caused by chloride binding. The most important mechanism for this is the formation of chloro-aluminates with the aluminate phases in cement. There are many arguments in favour of each coefficient for considering durability of structures. It can be argued that bound chlorides will not cause corrosion but it is also known that they can be released if the pH drops. However in this simple experiment neither measure will take account of ion-ion interactions.

The ASTM test is not normally used to get a diffusion coefficient. The result is simply given as charge passing. However the Nordtest uses the Nernst-Planck equation to get a coefficient and simple diffusion tests just use Fick's law. The effect of ion-ion interactions and the membrane potential is not normally used for any of them.

If the ASTM test is used for comparing mixes it can be seen from figures 5 and 6 that the result will be incorrect if pozzolanic mixes are compared with non-pozzolanic. In some specifications a maximum charge passing of 1000 Coulombs is specified and the mix design is left to the contractor.

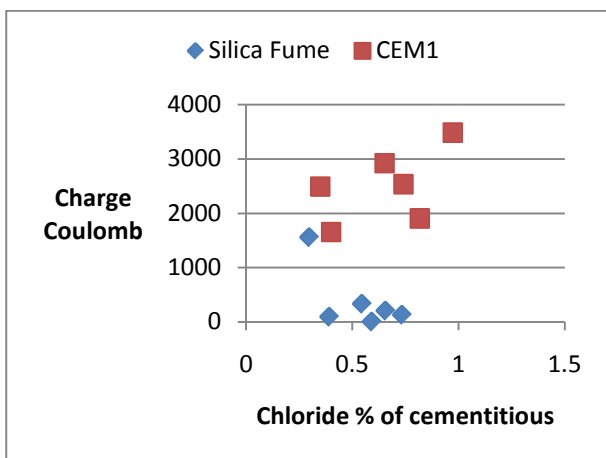


Figure 15. Comparison of Charge passing with data for a simple diffusion test for mixes with

w/c=0.3 and 20% silica fume replacement (Claisse 1988)

Figure 15 shows results with a range of mixes with similar properties indicated by a simple diffusion test. The pozzolanic mixes generally have Coulomb values below 1000 and the CEM1 mixes above. This data indicates that the ASTM C1202 test is not suitable for this purpose. The differences between figures 9 and 10 indicate that the Nordtest would also be unsuitable. However it should be noted that these two tests can be used very effectively for quality control purposes. If regular samples are taken from concrete used on site, a change in the result from the tests will clearly indicate a problem.

For modelling concrete durability it has been noted that neither the simple diffusion test nor the models take account of ion-ion interactions. It may also be seen that the simple diffusion test has a good resemblance to the geometry of an exposed concrete surface on site. It may therefore be indicated that results from the test may be used in the model subject to concerns about changing conditions which may affect adsorption or ionic concentrations. It is indicated that the use coefficients from electrical tests in these models should only be attempted if numerical simulations are used to correct for the effect of the applied field on the ion-ion interactions.

6. CONCLUSIONS

- All measurements of diffusion in concrete, with or without applied voltages, are significantly affected by ion-ion interactions.
- For the comparison of mixes with different cementitious materials in them a simple diffusion test should be used unless computer modelling is used to correct the results of electrical tests.
- The electrical tests are suitable for quality control purposes.
- For modelling the life of structures a diffusion coefficient which includes some "adjustment" for ion-ion interactions (such as that obtained by applying Fick's law to a simple diffusion test) should be used.

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