Simulation of the concrete chloride NT build-492 migration test

Numerical Modeling
Strategies for Sustainable Concrete Structures

Aix-en-Provence, France
May 29-June 1, 2012

J. Lizarazo-Marriaga[1], J. Gonzalez[1], P. Claisse[2],

[1] *Universidad Nacional de Colombia*
[2] *Coventry University- UK*

1 INTRODUCTION

Corrosion of steel reinforcement is the major cause of deterioration in concrete structures, and carbon dioxide and especially chlorides are the main causes of damage. The rate at which chloride ions diffuse through concrete is a major determinant of the durability of structures. If chloride ions reach the vicinity of the rebar, the passive film around the steel can start to break down and the process of corrosion begins.

The classical approach for ion transport in solutions states that if there is a difference in the concentration of ions in different regions, this gradient produces a flow of ions. Such a movement is called diffusion. In the same way, if there is a difference of electrical potential, this flow is called migration or electro-migration. The principle of electro-migration tests is to apply a constant potential difference across a fully saturated sample. Usually they are performed in two chamber cells with the concrete in the middle, and each cell full of a defined solution. As the chloride is the ion of interest and the pore solution of concrete contains sodium, potassium and hydroxyls, these species are the most commonly used to fill the cells.

The standard NT492 [1] is extensively used around the world to determine the chloride diffusion coefficient. It assumes that the chloride ions are isolated particles without any ionic interaction with other species. However, as chloride ions are charged particles, they interact with other species which affect the ionic flux. In order to investigate the chloride penetration numerically during a standard NT-492 experiment, simulations of the test have been carried out. For this, two different approaches have been used. First, the equations of the standard based on a mono-ion condition have been applied. Secondly, a finite difference coupled numerical multi-species model accounting for a binding isotherm and the ionic interaction caused by the species penetrating the sample or contained in the pore solution has been developed.

2 NT BUILD-492

2.1 Test description

This test method requires cylindrical specimens of 100 mm diameter and a thickness of 50 mm. An external electrical potential is applied across the sample in order to force the chloride ions to migrate into the concrete. After the test, the sample is split and a silver nitrate solution sprayed on to one of the sections. The penetration depth is measured from the chloride precipitation, and the migration coefficient can be calculated using equations given in the standard. The preconditioning of the samples before the test is similar to that of the ASTM C1202 standard [2]. The solutions used in the cathode and anode are a 10% NaCl and a 0.3 N NaOH respectively. Figures 1 and 2 show the arrangement of the migration set up.

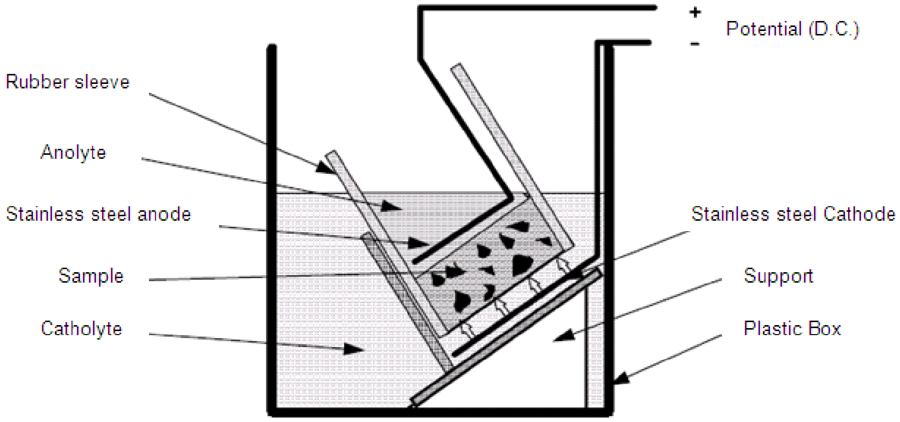

Figure 1 Arrangement of the migration test (NTBuild-492)

Figure 2 Experiment Set-up

2.2 Test theoretical background

The migration Nordtest NT492 has been used extensively to find the non-steady-state migration coefficient. The analysis in it is based on the Nernst-Planck equation for a chloride mono-ion system assuming a semi-infinite homogeneous medium. If there is a chemical potential or concentration gradient and an electrical field, the flux for ionic transport can be expressed as equation 1.

$$J = -D\frac{\partial c}{\partial x} - \frac{zF}{RT}Dc\frac{\partial E}{\partial x} \qquad (1)$$

where, D is the diffusion coefficient of species, z is the electrical charge, F is the Faraday constant [9.65 x104 Coulomb/mol], R is the gas constant [8.31 J/mol/^{o}K], T the absolute temperature [^{o}K], E the electrical voltage [V], C is the ionic concentration of the species in the pore fluid [mol/m^3], and x is the distance from the surface of the sample [m].

As electro-migration tests are carried out in laboratory facilities and the time is therefore limited to a few hours or days; the NT-Build 492 assumes that the diffusion term of the Nernst-Planck equation does not provide an important contribution to the total flux and can be considered to be negligible. Thus:

$$J_M = \frac{z_i F}{RT} D_i c(x,t) \frac{\partial E}{\partial x} \qquad (2)$$

The mathematical solution for the Nernst-Planck equation (2) can be obtained using the error function (*erf*) [3].

$$c(x,t) = \frac{c_s}{2}\left[e^{ax} ercf\left(\frac{x + aDt}{2\sqrt{Dt}} \right) + ercf\left(\frac{x - aDt}{2\sqrt{Dt}} \right) \right] \qquad (3)$$

where *ercf* is the complementary error function, c_s is the constant chloride concentration at the surface, and a is a constant related with the external voltage applied, defined by equation 4.

$$a = \frac{zF\varphi}{RT} \qquad (4)$$

In order to find the non-steady-state migration coefficient, the standard follows the recommendations of Tang and Nilsson [3]. It uses the mathematical solution for the Nernst-Planck equation for a chloride mono-ion system assuming a semi-infinite homogeneous medium. The equations given by the standard are summarized below.

$$D_{nssm} = \frac{RT}{zFE} \frac{x_d - \alpha\sqrt{x_d}}{t} \qquad (5)$$

$$E_f = \frac{U-2}{L}$$

$$\alpha = 2\sqrt{\frac{RT}{zFE}} erf^{-1}\left(1 - \frac{2c_d}{c_0} \right)$$

where D_{nssm} is the non-steady state migration coefficient, [m^2/s], U the absolute value of the applied voltage [V], T the average value of the initial and final temperatures in the anolyte solution [°K], L the thickness of the specimen [m], x_d the average value of the penetration depths [m], t the test duration [S], erf^{-1} the inverse of error function, c_d the chloride concentration at which the colour of the silver nitrate indicator changes ≈0.07N for OPC, c_0 the chloride concentration in the catholyte solution and E_f the electric field applied [V/m].

3. MULTI-SPECIES NUMERICAL MODEL

The multi-species computational model used in this paper was developed in the Construction Materials Applied Research Group of Coventry University [4]. It uses a finite difference method and simulates a sample of concrete under migration conditions. The numerical code works by repeated application of the Nernst – Planck equation through time and space; however, the flux for each ion resulting from the diffusion and migration conditions is balanced and affected by an additional electrical voltage (membrane potential) if a net charge builds up at any location. A detailed explanation about the implications of the membrane potential in a migration test has been presented by Lizarazo and Claisse [5].

The inputs for the model are as follows:

- The intrinsic diffusion coefficients for all the ions involved (usually given for chlorides, hydroxides, sodium and potassium).
- The concentration at the boundaries or external conditions (e.g. in the cell chambers).
- The concentration of the concrete pore solution.
- The ionic binder capacity factor (α) (usually given just for chlorides through a linear isotherm).
- The open porosity of concrete.
- The geometrical characteristics of the concrete sample (diameter and length).
- The external voltage applied.
- The duration of the test.

The outputs of the model are the following:

- The transient evolution of the total current carried for the sample, and the relative currents carried for each ion in any time.
- The non-linear membrane potential for any time and position
- The evolution of the fluxes and concentrations for each ion for any time and position

Once the fluxes and concentrations are calculated the model ensures that there is not charge build up throughout the sample at any time for all the ions together. If there is any charge build-up, the model corrects the actual migration flux until the charge balance is within a specified range ($< 10^{-12}$ Coulumbs). Macroscopically, the procedure to maintain the charge balance is according to Kirchoff's law: ".....the current density into any point will equal the current out of it". That means that at any time the total current in node i is equal to the current in node $i+1$. If at any time the charge surplus is bigger than the specific limit, the electrical field for all cells is changed in a specific proportion and the programme re-calculates the migration flux until the charge criterion is satisfied.

During a migration test the physical transport properties are unknown so an optimization technique was developed to calculate them from the results. This was achieved by running the model a number of times and using the results as a database in order to obtain the input data from known output. The optimization technique used was an artificial neural network algorithm (ANN). It was trained to optimize the principal related physical properties involved during a standard migration test. A detailed procedure has been published [6, 7]. The neural network model was constructed and trained using the neural network tool box of Matlab®. To train the network the numerical physical model was run a large number of times in order to obtain enough input vectors and the corresponding target vectors.

4. EXPERIMENTAL PROGRAMME

A single mortar mix having a water to cement ratio of 0.36, and a sand to binder ratio of 3 was cast. Ordinary Portland cement CEM I without mineral or chemical admixtures was used. The specimens were cured under lime water at 21 ±2 °C prior to testing. Table 1 shows the proportions of the materials used. Because of the low water to cement ratio the mix had a poor workability, and so it was compacted manually using prolonged tamping in order to reach its maximum density.

	kg/m3		
W/B	OPC	Sand	Water
0.36	650	1950	234

Table 1. Mortar mix design

Using experimental results and the neural network optimization model, the transport related properties for the mortar mix under test were calculated (Table 2). Details of the optimization algorithm and the procedure used to find the transport properties are in reference (4) and are outside the scope of this paper and will not be discussed.

Intrinsic diffusion coefficients				**Cl Binding Capacity**	**Open Porosity**	**Concentration OH$^-$**
D-Cl	**D-OH**	**D-Na**	**D-K**			
1.9E-10	7.9E-11	2.1E-11	4.1E-12	**0.38**	0.171	240

Table 2. Transport properties optimized

5. COMPUTATIONAL SIMULATION OF THE NORDTEST 492

Under special conditions, the results obtained from the multi-species numerical model are similar to those found using equation 3. Those conditions refer to the following assumptions.

- There is no ion interaction between different species (No voltage correction: no membrane potential is generated).
- There is no binding of any species.
- There is no depletion of the chloride concentration in the cathode reservoir during the test (this is simulated by using a very large reservoir volume).
- There are no ions in the pore solution in the sample at the start of the test.

In order to illustrate the theoretical concentration profiles of equation 3, the model was run using the inputs shown in table 3. The numerical values were established according the suggestions of the standard and the physical conditions stated above. Figure 3 shows the calculated chloride profiles for different times, which behave in a similar way to that described by Tang and Nilsson [3]. Under the influence of an electrical field, chlorides move by migration at a constant speed and therefore create a penetration front. The steady state is reached when the chloride concentration inside the sample no longer changes.

	Valence	Intrinsic Diffusion	Concentration [mol/m³] (in liquid)			Cl Binding Capacity factor
	z	D m²/s	negative	in sample	Positive	
Chloride	-1	1.90×10^{-10}	1900	0	0	1

No of cells:	500
Voltage correction?	**NO**
Time step [s]:	1
Run time [hours]:	8
Porosity:	1
Applied voltage [V]:	8

Sample length [m]	0.05
Sample radius [m]	0.05
Room temp [K]	295
Cell volumes [m³]:	1
Heat loss fact [J/K]:	0.3

Table 3. Inputs of the model

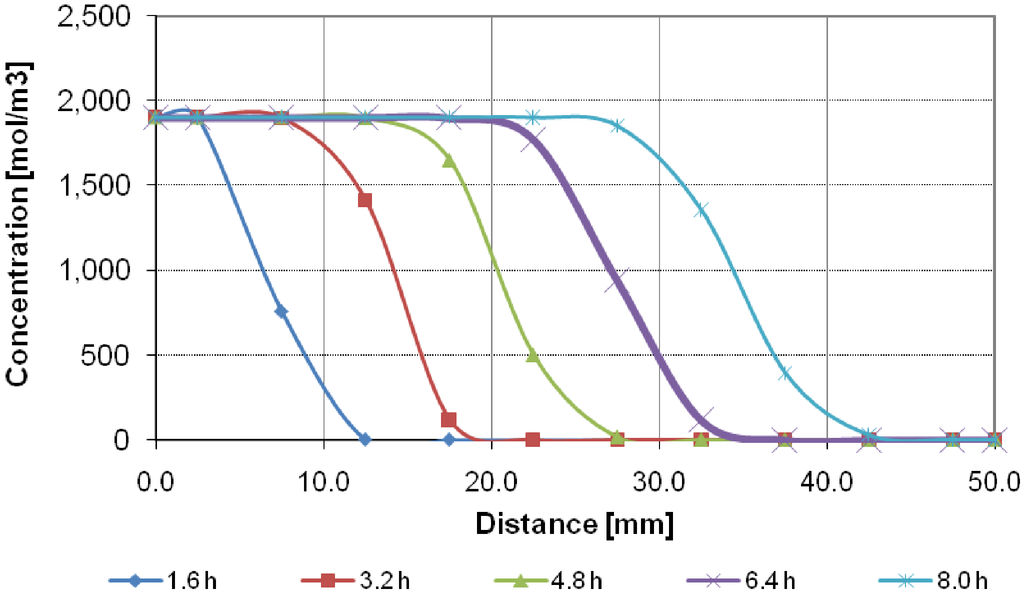

Figure 3 Theoretical concentration profiles for different times [h] (obtained from the computer model with no voltage corrections and thus the same as those from the analysis method in Nordtest 492)

In order to compare the theoretical chloride profiles from equation (3) with the profiles simulated by the computer model, including ionic interactions, the pore solution and chloride binding, a new simulation was carried out. The input data is shown in table 4, including the diffusion coefficients and the initial concentration of the species incorporated. Results of the model are shown in figure 4, which shows the evolution of chlorides for different times.

	Valence	Intrinsic Diffusion	Concentration [mol/m³] (in liquid)			Capacity factor
	Z	D m²/s	negative	in sample	positive	
Hydroxyl	-1	7.877E-11	0	239.973	300	0.171
Chloride	-1	1.904E-10	1900	0	0	0.383
Sodium	1	2.061E-11	1900	7.92E+01	300	0.171
Potassium	1	4.099E-12	0	1.61E+02	0	0.171

No of cells:	500
Voltage correction?	**YES**
Time step [s]:	1
Run time [hours]:	8
Porosity:	0.171
Applied voltage [V]:	8

Sample length [m]	0.05
Sample radius [m]	0.05
Room temperature [K]	295
Cell volumes [m³]:	0.03
Heat loss factor [J/K]:	0.30

Table 5. Input data for the multi-species model

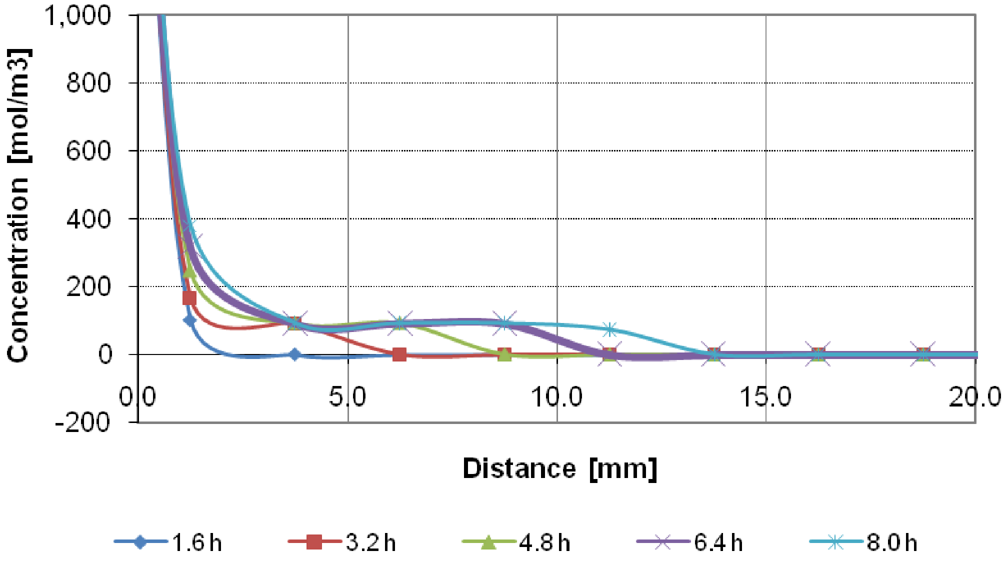

Figure 4. Multi-species model concentration profiles for different times [hours]

Using the concentration profiles obtained from the “virtual” migration test shown in figure 4, the non-steady state migration coefficient was determined (D_{nssm}) following the procedure suggested by the NT492. (The approximate relationships given by the standard to obtain the coefficient were presented in equation 4). For this, it was assumed that the test lasts for 6.4 hours, so, the chloride profile at this time had a penetration of 9.3 mm when the concentration was 70 mol/m^3 (x_d). This specific concentration was used because it is the concentration of free chlorides at the boundary when the colorimetric method is used. The chloride diffusion coefficient (D_{nssm}) obtained using the virtual x_d, according to the standard, gives a value of 5.23×10^{-11} m^2/s. This diffusion coefficient, which acts as a proportional parameter in equation 3, forces the profile to have an approximate concentration of free chlorides of 70 mol/m^3 at 9.3 mm, in the same way as the numerical model does.

Although the numerical model, which includes several physical parameters involved in the chloride transport phenomenon (pore solution, chloride binding and ionic interaction) and equation 3 had the same value of concentration (70 mol/m3) for a penetration of 9.3 mm, the profiles were very different.

It can be seen that although in the Nordtest the diffusion coefficients were found from a known value of penetration and concentration, the real profile obtained is different to that calculated using ionic interaction and binding. The penetration fronts expected by the standard were obtained, using in their model a single ion condition; in reality, of course, the situation is much more complex. Indeed, when the Nernst-Planck equation, adapted to account for ionic interactions is used, the penetration front does not behave in the way reported in the literature [3].

6. CONCLUSIONS

- The straightforward application of equation 3 to simulate chloride diffusion in concrete, which has been extensively in the past, can be significantly improved by using a numerical simulation which includes the effects of chloride binding, the concrete pore solution, and other ions different to chlorides into the system.
- The diffusion coefficients used in the multi-species model cannot be compared with others reported elsewhere unless they have been obtained using the same refinements to the analysis.

7. REFERENCES

[1] NTBUILD-492, NORDTEST METHOD: Concrete, Mortar And Cement-Based Repair Materials: Chloride Migration Coefficient From Non-Steady-State Migration Experiments. 1999.

[2] ASTM-C1202, Standard Test Method for Electrical Indication of Concrete’s Ability to Resist Chloride Ion Penetration. 2005.

[3] Tang, L. and L.-O. Nilsson, Rapid Determination of the Chloride Diffusivity in Concrete by Applying an Electric Field. ACI Materials Journal, 1992. 89(1): p. 49-53.

[4] Claisse, P.A., H.I. Elsayad, and E. Ganjian, Modelling the rapid chloride permeability test. Cement and Concrete Research, 2010. 40(3): p. 405-409.

[5] Lizarazo-Marriaga, J. and P. Claisse, Effect of the non-linear membrane potential on the migration of ionic species in concrete. Electrochimica Acta, 2009. 54(10): p. 2761-2769

[6] Lizarazo-Marriaga, J. and P. Claisse, Determination of the concrete chloride diffusion coefficient based on an electrochemical test and an optimization model. Materials Chemistry and Physics, 2009. 117(2-3): p. 536-543.

[7] Lizarazo-Marriaga, J. and P. Claisse, Determination of the transport properties of a blended concrete from its electrical properties measured during a migration test. Magazine of Concrete Research, 2010. 60(3): p. 163-175.