

Coventry
University

Coventry University Repository for the Virtual Environment (CURVE)

Author name: Claisse, Peter

Title: Effect of the non-linear membrane potential on the migration of ionic species in concrete

Article & version (e.g. post-print version): Final post-print version - refereed

Original citation: Marriaga, J. Lizarazo and Claisse, Peter A. (2008) 'Effect of the non-linear membrane potential on the migration of ionic species in concrete, *Electrochimica Acta*, Vol. 54 (10) 2761-2769

DOI: 10.1016/j.electacta.2008.11.031

Copyright © and Moral Rights are retained by the author(s) and/ or other copyright owners. A copy can be downloaded for personal non-commercial research or study, without prior permission or charge. This item cannot be reproduced or quoted extensively from without first obtaining permission in writing from the copyright holder(s). The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the copyright holders.

This document is the [e.g. author's final manuscript version] of the journal article, incorporating any revisions agreed during the peer-review process. Some differences between the published version and this version may remain and you are advised to consult the published version if you wish to cite from it.

Available in the CURVE Research Collection: January 2009

<http://curve.coventry.ac.uk/open>

Effect of the non-linear membrane potential on the migration of ionic species in concrete

Juan Lizarazo Marriaga^a, Peter Claisse^b

^a *Departamento de Ingeniería Civil, Universidad Nacional, Bogotá-Colombia*

^b *Construction Materials Applied Research Group, Coventry University COV 5FB, UK*

Abstract

In a concrete migration test the ionic species are present either in the boundary layer or in the pore solution and they flow as is indicated by the Nernst – Planck equation. This equation supposes that the flux of each ion is independent of every other one. However, due to ion-ion interactions there are ionic fields that affect the final flux producing an additional voltage known as the membrane potential. In order to understand this phenomenon, this paper describes a theoretical and experimental investigation of the implications of the membrane potential on the migration of chlorides in concrete. A new electrochemical test has been carried out and its results were compared with a numerical simulation. From the results it has been proved that the voltage drop during a migration test is not linear and changes during the test. Thus the Nernst-Planck equation may be applied to the simulation of migration of any ionic species through a saturated porous medium by using the non linear voltage to represent all the microscopic interactions in a macroscopic way. The results may be used to improve the reliability of the ASTM C1202 chloride migration test.

1. INTRODUCTION

The rate at which chloride ions can diffuse through concrete is strongly related to the corrosion of reinforcement in structures. If chloride ions reach the vicinity of the rebar,

the passive film around the steel bar can be broken and the process of corrosion can start. The mechanisms that control the penetration of chloride into saturated concrete are complex and understanding them is essential for the design assessment of durable reinforced concrete. When the ions move, their negative charge creates an electrostatic field which causes them to interact with other ions in the area. The other ions may be more chloride or other mobile species such as hydroxyl, sodium, or potassium. These processes will affect the transport of ions with or without an applied electric field.

Pure diffusion tests take long time; however, engineering and construction times are shorter. To solve this problem, pure diffusion can be accelerated by the application of an electrical potential gradient (migration tests). Under the influence of an electric field ions experience a force directing them toward the electrode that has the opposite charge to the ion [1]. The time needed to perform a pure diffusion test may be months; but, a migration test can be done in just days or hours. Thus there is a need to provide a better understanding of migration tests so the results may be interpreted more accurately.

The migration of ions into concrete is controlled by the following factors:

- The chemical potential of the ion (concentration gradient)
- The applied electrical potential (if it exists),
- The charge of the ion,
- The concentration of each species in the pore solution,
- The porosity and tortuosity of the pore network,

- The chemical reactions between the ions present in the porous and the cement hydration products. These reactions can either be of dissolution, decalcification or binding [2], [3].

The particular concern when testing concrete is that a durable concrete in which chlorides do not penetrate the cover layer will have low porosity, high tortuosity and high binding capacity. When a pozzolanic admixture is added it will react with the free lime and reduce the hydroxyl ion concentration. This will reduce the measured migration current but will not necessarily make the concrete more durable because the porosity, tortuosity and binding may be unaffected.

Different approaches have been used in recent years to model the ionic penetration of chlorides through concrete. In order to understand this phenomenon, this paper reports on a theoretical and experimental investigation to give a better explanation for the movement of chloride ions and any other species in concrete under the influence of an applied electric field. The principal research was to determine the voltage within a sample during the ASTM C1202 rapid chloride test by simulating the movement of ions. The results of the experimental program were compared with these numerical simulations. The nonlinear behaviour of the electrical field during normal diffusion and migration has been reported previously by some researchers [4]-[5],[6], however, the authors are not aware of any experimental evidence for it. The only reference found for this was the work made by Zhang et al. [7], [8] who measured the total membrane potential across a sample of concrete in a diffusion test.

Research Objectives

In summary, the objectives of this work are as follows:

- 1 To develop a theoretical explanation for the movements of chloride ions in concrete under the influence of an applied electric field.
- 2 To use the theory to calculate the evolution of the voltage within a sample during the ASTM C1202 rapid chloride test.
- 3 To provide an experimental validation of the theory when applied to the ASTM C1202 test
- 4 To enable the problem with the ASTM C1202 test to be overcome. This problem gives misleadingly low results if pozzolanic admixtures such as pulverised fuel ash or silica fume are added to concrete.

The method to be validated in (3) calculates the mid-point voltage at different times from the known properties of the sample, particularly the chloride diffusion coefficient. To achieve the final objective (4) it is necessary to calculate the properties from observations of the voltage. This may be 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. This may, for example, be achieved with an Artificial Neural Network which is trained using output from the model.

1.1 Modelling the migration test

In a fully saturated concrete sample there may be a difference in the concentration of ions in different regions. If a constant electric potential is applied, as in the ASTM C1202 (RCPT) test [9] or NT-492 [10], the total flux J_i for each species in the system must be the sum of the migration flux $(J_M)_i$ and the diffusion flux $(J_D)_i$.

$$J_i = (J_M)_i + (J_D)_i \quad \text{Equation 1}$$

The diffusional flux due to a concentration gradient in a solution has been known empirically since 1855 as Fick's first law [11].

$$\text{Equation 2}$$

where J_i is the flux of species i [mol/m²/s], D_i is the diffusion coefficient of species i [m²/s], c_i is the ionic concentration of species i in the pore fluid [mol/m³], and x is the distance [m].

In an ideal solution the driving force for diffusion can be considered in terms of the chemical potential of the particular species. In the same way, the driving force for migration is proportional to the external electric field. In an electrolytic system under a difference of potential, the transport of charge is ionic transport. The migration flux of species i is defined in equation 3 [12].

$$\text{Equation 3}$$

where u_i is the mobility of species i in the pore fluid [m² s⁻¹ volt⁻¹], z_i is the electrical charge of specie i , F is the Faraday constant [9.65 x10⁴ Coulomb/mol], and E is the electrical potential [V]. In the same way, the diffusion coefficient is proportional to the mobility of each ion [1].

$$D_i = RTu_i \quad \text{Equation 4}$$

The general law governing the ionic movements in concrete is considered to be due to the chemical and electrical potential [13], and is known as the Nernst-Planck equation:

$$J_i = -D_i \frac{\partial c_i}{\partial x} - \frac{z_i F}{RT} D_i c_i \frac{\partial E}{\partial x} \quad \text{Equation 5}$$

where R is the gas constant [8.31 J/mol/°K] and T is the absolute temperature [°K]. The Nernst-Planck equation supposes that the flux of each ion is independent of every other one; however, due to ion-ion interactions there are ionic fields that affect the final flux. The drift of a species i is affected by the flows of other species present. The law of electroneutrality ensures that no excess of charge is introduced [1]. Under a concrete migration test, the current density into any point will equal the current out of it (Kirchoff's law).

$$0 = F \sum_i z_i J_i \quad \text{Equation 6}$$

Faraday's law states the equivalence of the current density (i_i) and the ionic flux.

$$\text{Equation 7}$$

In an electrolyte solution in which concentration gradients of the ionic species and an electrical field are present, the total current density (i_T) is equal to the sum of the current density produced by the diffusion and the migration conditions.

$$i_T = -\sum_i z_i F (J_D + J_M)_i \quad \text{Equation 8}$$

The total current can be given by a combination of equations 2 and 3.

$$i_T = \sum_i z_i F R T u_i \frac{\partial c_i}{\partial x} + \sum_i z_i^2 F^2 u_i c_i \frac{\partial E}{\partial x} \quad \text{Equation 9}$$

The electric potential gradient is given by two terms: a linear or ohmic potential and a non-linear or membrane potential.

$$\frac{\partial E}{\partial x} = \underbrace{\frac{i_T}{\sum_i z_i^2 F^2 u_i c_i}}_{\text{Ohmic potential}} - \underbrace{\frac{\sum_i z_i F R T u_i \frac{\partial c_i}{\partial x}}{\sum_i z_i^2 F^2 u_i c_i}}_{\text{Membrane potential}} \quad \text{Equation 10}$$

The first term is related to the ohmic potential when an external voltage is applied and is characteristic for charge transfer accounting exclusively the migration driving forces. The second term of Equation 10 is that for the membrane potential gradient $\delta E_p / \delta x$, formed when various charged species have different mobility. In a concrete migration test the nonlinearity of the electric field is due to the membrane potential gradient and it is equivalent to the liquid junction potential [4].

$$\text{Equation 11}$$

Likewise, the electric field due to the diffusion potential can be expressed in terms of the transference number (t_i) [3].

$$\frac{\partial E_p}{\partial x} = \frac{RT}{F} \sum_i \frac{t_i}{z_i} \frac{\partial \ln c_i}{\partial x} \quad \text{Equation 12}$$

The non linearity of the electric field in a migration test can be explained from a physical point of view. At the start of the test the field is uniform across the concrete, however, when the different ions start to migrate they can not move freely, they are charged particles and interact with species of opposite signs. The membrane potential affects the electric field across the concrete and its effect over the sample can be explained in term of resistances. Each point into the concrete sample has a changing resistivity as the free and adsorbed ionic concentrations in it change during the test.

2. REVIEW OF MODELLING OF THE CHLORIDE DIFFUSION-MIGRATION

Different approaches have been proposed in order to simulate the penetration of chloride into the concrete taking into account all the different species and an external electrical driving force. Truc et al. [14] proposed a numerical model based on a finite difference method for the flux of several species with the Poisson - Nernst - Planck equations. Sugiyama et al. [2] presented a method for numerically calculating the concentration profiles of chloride ions (Cl^-) in concrete; the method is based on the generalized form of Fick's First Law suggested by Onsager [2]. Narsilio et al. [15] simulated electromigration tests solving the Nernst–Planck equation coupled with the electroneutrality condition using a finite element method. Khitab et al. [5] developed a numerical model to predict the chloride penetration solving the Nernst–Planck equation coupled with the current laws. A numerical model was developed by Claisse [16] using the Nernst – Planck equation and maintaining charge neutrality by modelling changes to the voltage distribution. Lorente et al. [4] showed a model

based on a second-order finite difference procedure that solves the law of mass conservation equation for each species and an electrical field equation for the overall system. Samson et al. [17] presented a model to solve the transport of ions in saturated materials during a migration test using a finite element method. More recently, Krabbenhoft [6] solved the Poisson - Nernst – Planck equations analytically and derived an expression for the diffusion using a nonlinear finite element procedure.

The assumption that the electrical field remains constant under a migration test has been pointed out by many researchers [15] and standards [10], [18]. However, the electrical field can be accounted for in a macroscopic way from equation 11 [4], [5]. A more complex expression can be found for the electrical field, if the Nernst – Planck includes a chemical activity coefficient (γ) [19], however, it has been showed that the activity term does not increase the accuracy of the results in a concrete migration test [17], [20].

In a migration test the species present either in the boundary layer or in the pore solution of the sample (Na^+ , K^+ , Ca^+ , OH^- , and Cl^-) flow as is indicated by the Nernst – Planck equation. An increase in concentrations at specific points in the sample leads to variations in the electric field and the variation in the electric fields lead to variations in the flux of each ion. In the same way, the concentration and chemical composition of the pore structure of concrete at the start of the test are very important factors that need to be considered during the simulation. Truc et al. [14] found big differences in the migration of chlorides when the composition of the pore solution is included in the model.

From a microscopic point of view, the diffusion of chlorides can be affected by the effect of ionic interaction with other ions present into the pore solution and the effect of the known electrical double layer [21]. For a diluted solution, the ion – ion interaction produces a change in the chemical potential. The *Debye Huckel theory* [1] can be used as a qualitative tool in order to understand the phenomenon. The effect of the electrical double layer during diffusion is the generation of an additional electrical voltage at the interface between the pore wall and the pore solution [22]. Castelote et al. [23] found that during a migration test the effect of the electrical double layer does not seem to change the electrostatic interactions between the surface of the pores and the ions under migration.

From a macroscopic and engineering point of view, in normal diffusion the effects of the ionic interaction and the electrical double layer affect the mobility of chlorides generating a membrane electrical potential which may be opposed to the chemical potential. As was pointed out by Lorente et al. [4], the Nernst Planck equation must be used in natural diffusion (i.e. with no applied voltage) instead of Fick's laws in order not to neglect the effect of the membrane potential.

The numerical model used in this research was developed in the Construction Materials Applied Research Group of Coventry University [16]. It works by repeated application of the Nernst – Planck equation through time and space. To avoid discontinuities in the results the time step is reduced so the concentration does not change by more than 10% during any time step. The model was proposed for four ions in the pore solution, but can be easily changed to each number of ions. The transport processes into the concrete were restricted by binding with linear isotherms.

A linear isotherm defines a linear relationship between free and the bound ions over a range of concentration at a given temperature.

The effects of voltage changes in a migration test are applied in the model by distorting the voltage in each space step and checked by ensuring that charge neutrality is maintained throughout the sample at all times for all the ions together. At each time step adjustments are made to ensure that the total voltage across the sample is correct. Ion generation and removal at the electrodes is represented in the model by assuming that the ions being generated and removed are always hydroxyl ions. The model includes provision for the depletion on the reservoirs at either side of the sample. A conceptual diagram of the model is shown in figure 1.

3. EXPERIMENTAL PROGRAM

3.1 New experiment

An experimental program has been carried out to understand the voltage drop in a migration test and in order to investigate the influence of the nonlinear membrane potential in the diffusion of ionic species. The experimental results were used to validate and calibrate the numerical model used in this paper.

The apparatus used in this research was similar to ASTM C1202, but salt bridges were added in the concrete to check the voltage distribution across the sample (Figure 2). 4 mm diameter holes were drilled in each sample 5-8 mm deep. The salt bridge pipes were 4.5 mm dia. and were inserted into each hole. The salt bridges used a solution of 0.1 M of potassium chloride (KCL) because both ions in it have

similar mobility so no significant voltage would be set up at the interface of the salt solution and the concrete pore solution. In a previous research, Zhang et al. [8] measured the membrane potential across OPC mortar specimens during a diffusion test using reference electrodes and salt bridges in external cells. They found that for different simulated pore solutions the total junction potentials formed between the measurement devices and the simulated pore solution were in the range of -0.8 and -6 mV. Those values were relatively low compared with the membrane potential measured during the migration tests, so, the liquid junction potential formed between the salt bridge and the pore solution concrete sample was not be taken account in the research reported in this paper.

The voltage was measured relative to the cathode using a saturated calomel electrode (SCE) connected to the salt bridge. For each test, the current across the concrete and the voltage at different points in the sample were measured continuously with a data logger. The tests were carried out in a temperature controlled room at 21 ± 2 °C. During the tests the temperature was measured continuously in the anodic reservoir. Figure 2 shows the cell and the salt bridge. The volume of the anode and cathode chambers with the concrete sample ready for the tests was approximately 200ml.

A 3 Amp, 70 V programmable DC power supply was used. The data logger had 16 analogue inputs with 12-bit resolution, (0-2.4 V SE or ± 2.4 V Diff). A very high input impedance was required in order to ensure that the measuring process did not change the voltage readings. The internal resistance of the data logger had to be significantly greater than the resistance of the concrete during the test, because when measuring voltages the resistance of the equipment itself has an effect on the

voltage of the circuit. To achieve the required analog input performance of the data logger, it had a high resistance voltage divider followed by an operational amplifier configured as a voltage follower.

3.2 Material and test procedures

Mixes of mortar with water to cement ratio of 0.49 (Mix 1) and 0.65 (Mix 2) were cast. Ordinary Portland cement CEM I without mineral or chemical admixtures was used. The ratio binder / sand was 2.75 for all mixes. For each mix five cylinders of 100 mm diameter and 200 mm height were made to be used in porosity and migration tests. The open porosity accessible by water (P) was measured using the simple method of water displacement. The central part of each cylinder (30 mm thickness) was vacuum saturated until constant weight and weighed in water (W_w) and air (W_a). They were then dried in an oven at 105°C until constant weight and weighed again (W_d). The porosity was found with equation 13. Three replicates were tested for each mix. In addition, three 50mm cubes for each mix were cast in order to measure the mortar strength.

Equation 13

The specimens were cured under controlled humidity and temperature and all the migration tests were made at ages between 28 and 38 days. The concrete cylinders cast (100 mm diameter and 200 mm high) were cut to 50 mm thick and 100 mm diameter. Two samples were taken of each cylinder, being taken from its central part. The test was run on two replicate samples and the reported result is the average of both results. The anode and cathode reservoir cells were filled with a 0.30 N NaOH

and a 3.0% NaCl solution respectively (as specified in ASTM C1202), and a DC voltage of 30 volts were applied for 21 hours. This voltage was lower than the specified in the ASTM standard because 60 V caused unacceptable heating. The current was monitored every 2 minutes as well as the potential difference between the salt bridges in the sample and the negative electrode of the system.

For both mixes the voltages were measured at three different positions. The target location of those points was the mid point and the quarters of each sample. The distance between the points where the potential was measured and the edge of the sample in contact with the negative electrode (cathode) is shown in figure 3. The locations of the salt bridges define four zones named as Z1, Z2, Z3 and Z4 and the electric potential difference across each one was measured.

As at the start of the test the electric field is linear across the sample. The gradient or difference between the measured voltage at any time and the linear condition can be calculated. This value corresponds to the membrane potential and is calculated by subtracting the value of the voltage measured from the initial value measured at the start of the test for each time and position.

$$\Delta V = V_{Ti} - V_0 \quad \text{Equation 14}$$

ΔV corresponds to the membrane potential, V_{Ti} is the voltage measured at time t , and V_0 is the voltage at the start of the test. In order to avoid the noise found experimentally during the logging of the tests a commercial curve fitting software was used. It was found that this noise was substantially reduced by slightly increasing the depths of the drilled holes for the salt bridges. This observation indicates that the

noise was caused by the random distribution of aggregate limiting the contact between the salt bridges and the pore volume.

4. RESULTS AND DISCUSSION

4.1 Experimental results

The Results of strength and porosity are shown in table 1. Figure 4 shows the variation of the voltage across the sample in the mixes tested. Points E1, E2, and E3 are the points where the voltage was measured at the quarters and the mid point of the sample. Although for all the samples there was noise in the voltage, there is a good defined trend and the profile for the replicates in each mix were very similar. The voltage for each sample was not linear with respect to time and position during the test and the profile was related with the features of the sample and the conditions of the test.

The behaviour of the membrane potential across the sample during the test is shown in the figures 5 and 6 as contour graphs, each graph represents the average of two samples. The value for the membrane potential at the edges of the sample was assumed as zero because those points correspond to the electrodes in the solutions. Both mixes showed a similar distribution of the membrane potential. There was an increase of voltage in the area that was near to the alkaline solution (positive electrode) and both mixes reached a maximum value of voltage with a subsequent reduction. In the area near to the cathode, the membrane potential either tended to be constant during the test or presented a smooth negative variation.

From the contour plots all the membrane potentials at any point throughout the duration of the test can be seen. However tests of this type are expensive and not easy to complete. As alternative, it has been proposed to study just the behaviour of the mid point as a source of additional information in a practical situation. It is expected that the mid-point voltage would provide sufficient information for most practical purposes.

4.2 Simulation of the migration tests

In order to validate the numerical model both migration tests were simulated. The test for mix 1 ($w/b=0.49$) was selected as initial comparison and in the simulation of mix 2 ($w/b=0.65$) the value of the porosity was adjusted to obtain the value measured experimentally. The characteristics of the system sample/cells are shown in table 2. For this particular simulation, the initial pore solution concentration was based on published results [24]. The intrinsic diffusion coefficients for all the ions were obtained applying for the mix 1 an optimization process. The computer program was run enough times to find the best combination of coefficients to fit the experimental values of current and membrane potential in the mid point of the sample.

The intrinsic diffusion coefficients for sodium and potassium found were significantly lower than the values for chlorides and hydroxides as observed previously by other researchers [8], [13]. Those results confirm that the mobility of cations in porous media has a different behaviour than when they diffuse in an ideal solution. In the same way, the observed intrinsic diffusion coefficients for chlorides and hydroxides show that both ions are responsible for the most transport of charge, however, small changes in the diffusion of cations produce large changes in the mid point membrane

potential. Although the ratio of the intrinsic diffusion coefficients of chloride and hydroxide was greater than 1, it is apparent that the high mobility of chlorides is reduced in the computer model through the interactions between the ions and the hydration products of concrete using a linear isotherm.

The total electrical current through the samples is shown in figure 7 where the experimental results are presented with the simulations for mixes one and two. For mix 1 - the current modelled was presented both with the membrane potential and without any voltage correction. The experimental results and the simulation with the membrane potential were in good agreement, being better for initial times than for long times; the difference between them at the end of the tests was around 35 percent. In contrast, the profile of the current without including the membrane potential showed big differences respect to the experimental results. Although the initial current was similar, there was a maximum value of current three times greater than when was the voltage corrected. The current passed by mix 2 presented a similar profile for the experimental results and the simulations with the membrane potential corrections. As was expected, the last mix showed higher values of current because of its higher water cement ratio.

The behaviour of the simulated membrane potential of mix 1 across the sample and during the test is shown in figure 8 as a contour graph. The numerical values were taken from the numerical program and plotted with the contour function of Matlab®. The simulated membrane potential behaves in the same way as the corresponding experiment (figure 5). The voltage was negative in the first half of the sample during all the experiment; in contrast, the second half of the sample had positive values of membrane potential. The simulated and measured mid point membrane potential is

showed in figure 9 for mix 1. Although the measured profile showed some initial negative values and reached a local maximum membrane potential voltage before the simulations, both graphs showed similar behaviour and have same profile. From a macroscopic point of view, the local maximum or any feature of the mid point membrane potential can be explained as a result of the variation of the conductivity of the pore solution due to the migrations of all ions involved. The transient conductivity is defined by the relationship between the transient voltage and the transient current at any point.

The model can be optimized to predict the transport properties of any specific mortar or concrete mix. This may be 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. This may, for example, be achieved with an Artificial Neural Network which is trained using output from the model, so that a transient current and a transient membrane potential measured experimentally can be used to calculate the diffusion coefficients for all the ions involved during the test.

Although the principal aim of the computer model is simulate the chloride penetration, the profile of the other ions is calculated as result of the interaction between them. The relationship between the transport properties of the chlorides and the hydroxide ion has been recognised for long time ago, however, the transport of potassium and sodium in concrete is not extensively studied in the literature. Figure 10 shows the profiles of concentration for the four ions used during the simulation of mix 1.

5. CONCLUSIONS

- From the experimental program carried out and from the simulations made, the membrane potential was simulated and it has been proved that the voltage drop in concrete samples during a migration test is not linear with respect to time and position. The application of the Nernst-Planck equation to the simulation of migration of any ionic species through a saturated porous medium accounting for the non linear voltage allows models to include all the microscopic interactions in a macroscopic way.
- All the ions (sodium, potassium, hydroxide and chlorides) present in a migration test, either in the pore solution or coming from the external cells, need to be included in the simulation in order to account the non linear effects caused by differences of mobility. The computer model proposed predicts in a proper way the transient current and the membrane potential during the experiments.
- This model may be used to solve the problem with the ASTM C1202 procedure which occurs when it is used to test concrete with pozzolanic admixtures.

6. ACKNOWLEDGEMENT

The authors would like to thank the support of the Universidad Nacional de Colombia and the Programme Alβan (the European Union programme of High Level Scholarships for Latin America, scholarship No. E06d101124CO).

7. REFERENCES

1. Bockris, J. and A. Reddy, *Modern Electrochemistry 1 Ionics*. 1998: Plenum Press.
2. Sugiyama, T., W. Ritthichauy, and Y. Tsuji, *Simultaneous Transport of Chloride and Calcium Ions in Hydrated Cement Systems*. *Journal of Advanced Concrete Technology*, 2003. **1**(2): p. 127-138.
3. Yang, C.C., *On the relationship between pore structure and chloride diffusivity from accelerated chloride migration test in cement-based materials*. *Cement and Concrete Research*, 2006. **36**(7): p. 1304-1311.
4. Lorente, S., et al., *The single-valued diffusion coefficient for ionic diffusion through porous media*. *J. Appl. Phys*, 2007. **101**(024907).
5. Khitab, A., S. Lorente, and J.P. Ollivier, *Predictive model for chloride penetration through concrete*. *Magazine of Concrete Research*, 2005. **57**(9): p. 511-520.
6. Krabbenhoft, K. and J. Krabbenhoft, *Application of the Poisson-Nernst-Planck equations to the migration test*. *Cement and Concrete Research*, 2008. **38**(1): p. 77-88.
7. Zhang, J.Z. and N.R. Buenfeld, *Presence and possible implications of a membrane potential in concrete exposed to chloride solution*. *Cement and Concrete Research*, 1997. **27**(6): p. 853-859.
8. Zhang, J.Z., J. Li, and N.R. Buenfeld, *Measurement and modelling of membrane potentials across OPC mortar specimens between 0.5 M NaCl and simulated pore solutions*. *Cement and Concrete Composites*, 2002. **24**(5): p. 451-455.

9. ASTM-C1202, *Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration*. 2005.
10. NTBUILD-492, *NORDTEST METHOD: CONCRETE, MORTAR AND CEMENT-BASED REPAIR MATERIALS: CHLORIDE MIGRATION COEFFICIENT FROM NON-STEADY-STATE MIGRATION EXPERIMENTS*. 1999.
11. Basheer, P.A.M., *Permeation Analysis*, in *HANDBOOK OF ANALYTICAL TECHNIQUES IN CONCRETE SCIENCE AND TECHNOLOGY*, V.S. Ramachandran and J.J. Beaudoin, Editors. 2001, NOYES PUBLICATIONS.
12. Hamann, C.H., A. Hamnett, and W. Vielstich, *Electrochemistry* 2007.
13. Andrade, C., *Calculation of chloride diffusion coefficients in concrete from ionic migration measurements*. *Cement and Concrete Research*, 1993. **23**(3): p. 724-742.
14. Truc, O., J.-P. Ollivier, and L.-O. Nilsson, *Numerical simulation of multi-species transport through saturated concrete during a migration test -- MsDiff code*. *Cement and Concrete Research*, 2000. **30**(10): p. 1581-1592.
15. Narsilio, G.A., et al., *Comparative study of methods used to estimate ionic diffusion coefficients using migration tests*. *Cement and Concrete Research*, 2007. **37**(8): p. 1152-1163.
16. Claisse, P.A. and T.W. Beresford, *Obtaining More From the Electrical Chloride Test*. ACI - SP170-57, 1997. **170**.
17. Samson, E., J. Marchand, and K.A. Snyder, *Calculation of ionic diffusion coefficients on the basis of migration test results* *Materials and Structures*, 2003. **36**(3): p. 156-165.
18. JSCE-G571, *Test method for effective diffusion coefficient of chloride ion in concrete by migration*. 2003, Japan Society of Civil Engineers.

19. Truc, O., *Prediction of Chloride Penetration into Saturated Concrete - Multi - Species - Approach*, in *Department of Building Materials*. 2000, Chalmers University: Goteborg, Sweden.
20. Tang, L., *Concentration dependence of diffusion and migration of chloride ions: Part 2. Experimental evaluations*. *Cement and Concrete Research*, 1999. **29**(9): p. 1469-1474.
21. Zhang, T. and O.E. Gjorv, *Diffusion behavior of chloride ions in concrete*. *Cement and Concrete Research*, 1996. **26**(6): p. 907-917.
22. Friedmann, H., et al., *A direct method for determining chloride diffusion coefficient by using migration test*. *Cement and Concrete Research*, 2004. **34**(11): p. 1967-1973.
23. Castellote, M., et al., *Oxygen and chloride diffusion in cement pastes as a validation of chloride diffusion coefficients obtained by steady-state migration tests*. *Cement and Concrete Research*, 2001. **31**(4): p. 621-625.
24. Bertolini, L., et al., *Corrosion of Steel in Concrete: Prevention, Diagnosis, Repair* 2004: Wiley.

FIGURES

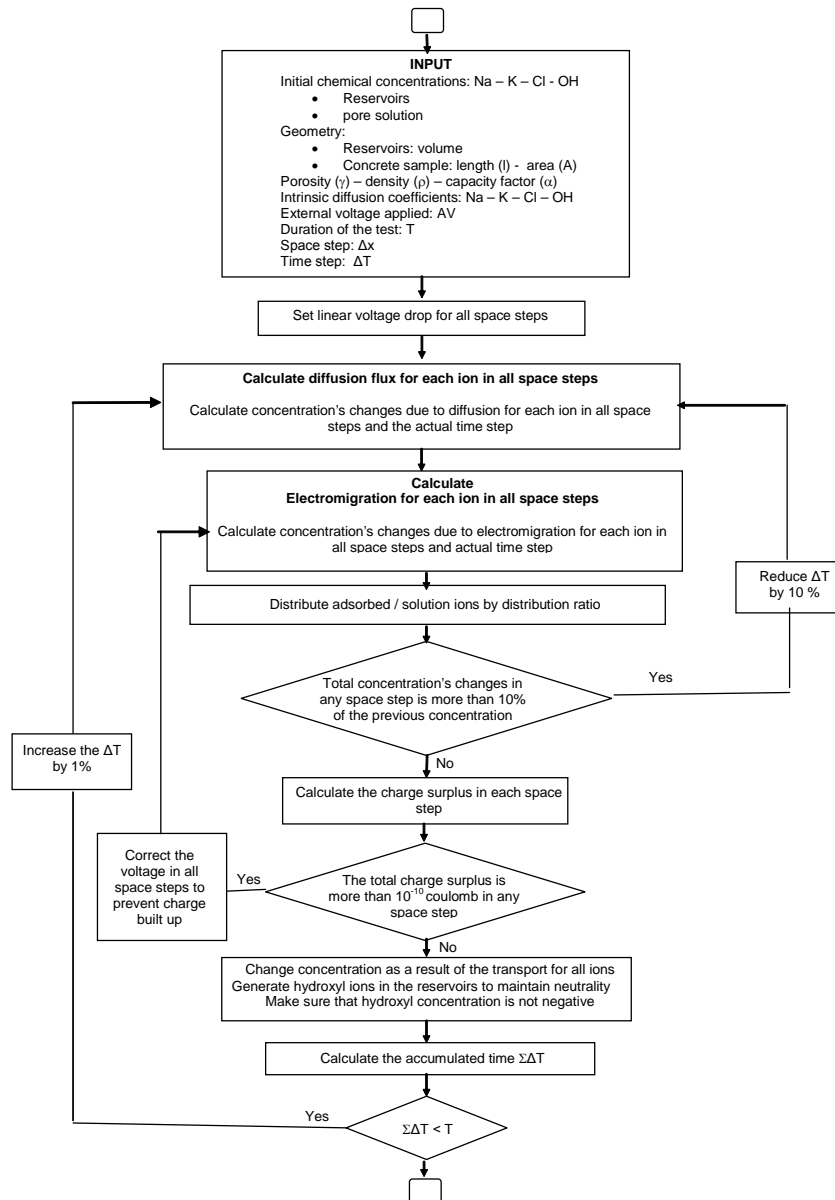


Figure 1 Computer Model used in this research

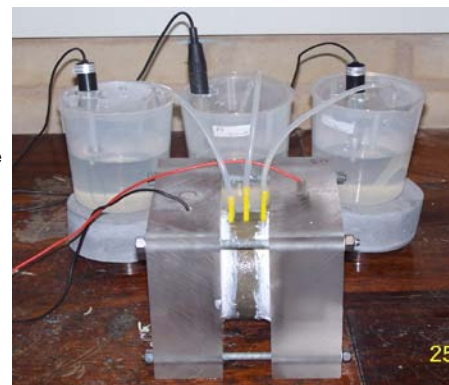
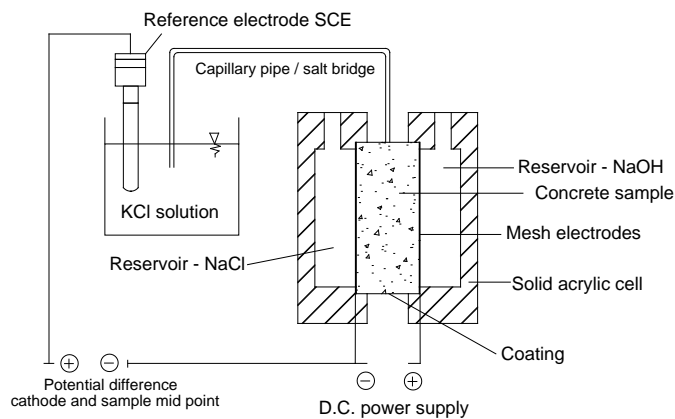


Figure 2 Cell and salt bridge

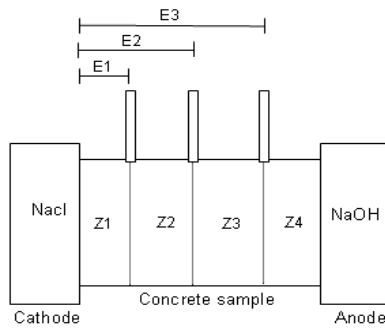


Figure 3 Target locations of the points where the voltage was measured

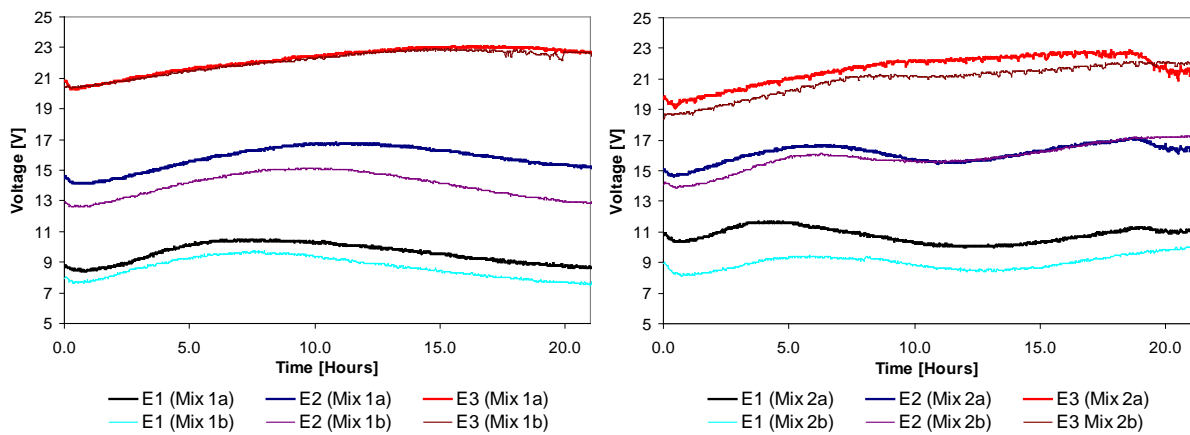


Figure 4 Difference of potential across the sample

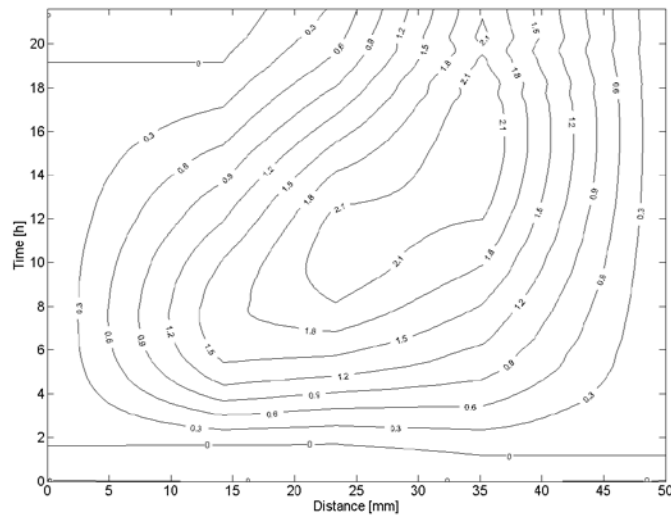


Figure 5 Average membrane potential mix 1– $w/b = 0.49$

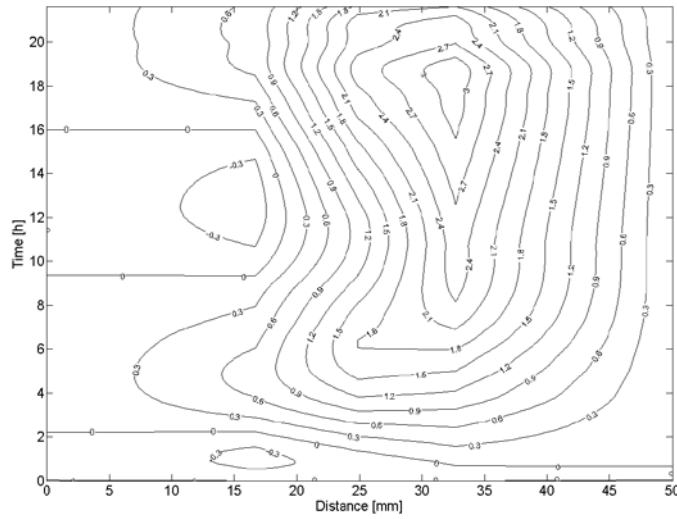


Figure 6 Average membrane potential mix 2- w/b = 0.65

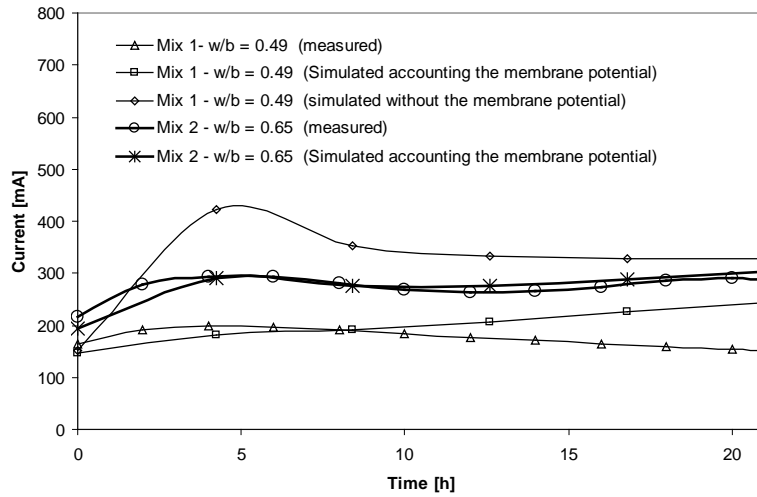


Figure 7 Current variations during the experiments

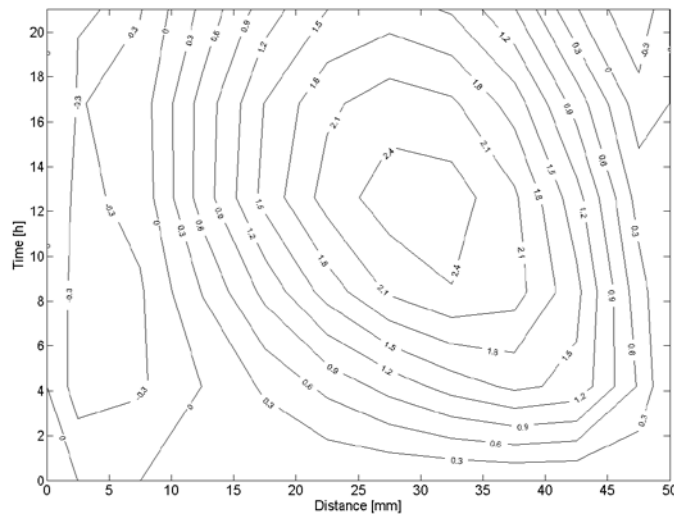


Figure 8 Simulated membrane potential [V] (mix 1 - w/b = 0.49)

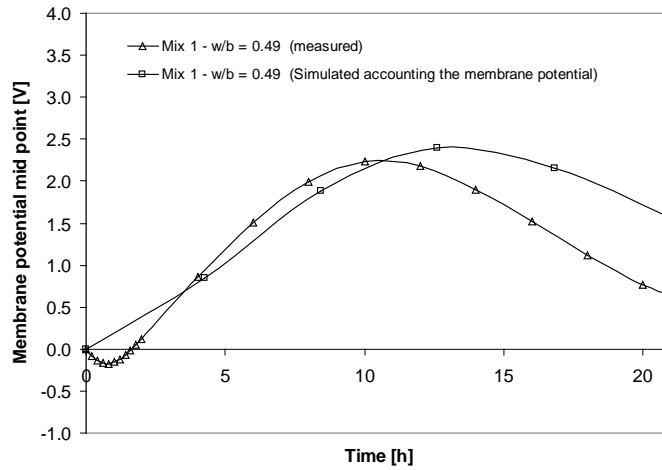


Figure 9 Simulated membrane potential mid point (mix 1 – w/b = 0.49)

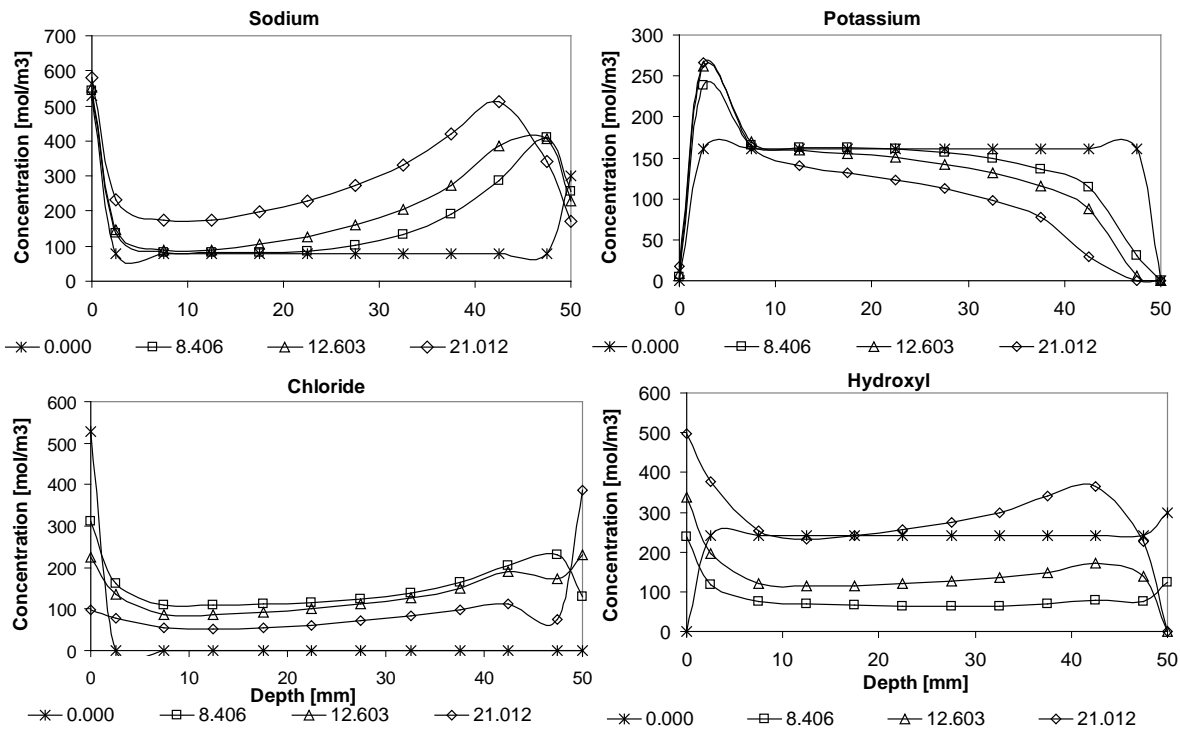


Figure 10 Concentration across the sample, distances from negative side in depth in mm vs. concentration in mol/m³ (mix 1 – w/b = 0.49)

Mix	water/binder	Concrete strength (28 days) [MPa]	Open porosity [%]
1	0.49	36.59	18.5
2	0.65	31.48	25.4

Table 1 Results of compressive strength and porosity

	Intrinsic Diffusion D [m ² /s]	Concentration [mol/m ³] Upstream (negative)	Concentration [mol/m ³] Pore solution	Concentration [mol/m ³] Downstream (positive)
hydroxyl	1.60E-10	0	240	300
chloride	3.00E-10	529	0.0	0
sodium	4.00E-11	529	79	300
potassium	9.00E-12	0	161	0
Sample length / radius [m]:	0.05 / 0.05		Run time [hours]:	21
Ext. voltage [V]:	30		Porosity:	0.19
Cell volumes [m ³]:	0.0002		Cl Capacity factor	0.3

Table 2 Input parameters at the start of the test.