

## **DETERMINATION OF THE CHLORIDE TRANSPORT PROPERTIES OF BLENDED CONCRETES FROM A NEW ELECTRIC TEST**

Juan Lizarazo Marriaga<sup>(1)</sup>, Peter Claisse<sup>(2)</sup>

<sup>(1)</sup> Departamento de Ingeniería Civil, Universidad Nacional, Bogotá-Colombia

<sup>(2)</sup> Construction Materials Applied Research Group, Coventry University CV1 5FB, UK

### **Abstract**

This paper describes methods to measure the movement of chloride in concrete, which causes corrosion of steel reinforcement. The general law governing ionic movements in concrete due to the chemical and electrical potential is known as the Nernst-Planck equation. In a migration test, because of the ion-ion interactions, there are ionic potentials that affect the flux producing a non-linearity of the electric field. These keep the electroneutrality of the species involved. This paper summarises a theoretical and experimental investigation of the application of these electric membrane potentials and the electrical current to the simulation of the migration of chlorides in concrete. A new test used to measure the membrane potentials has been developed and carried out with samples of concrete blended with Fly ash (FA) and ground granulated blast furnace slag (GGBS). A numerical model using the classical equations, but including changes in the voltage distribution through the concrete was optimised using an artificial neural network (ANN) model. Based on the experimental results and the simulations, the intrinsic diffusion coefficients of all the species were obtained. Also, the hydroxide composition of the pore solution, the porosity and the chloride capacity of binding were determined and compared with values from the model.

### **1. INTRODUCTION**

Due to very significant problems with reinforcement corrosion the penetration of chloride ions in concrete has been studied intensively for more than 40 years worldwide. As a result, physical models and experiments are well established. However, with the advent of more powerful computers, new numerical and experimental techniques are being applied to the solution of the complex problem of chloride penetration. This paper reports a research programme aimed at giving a better understanding of the phenomena involved in the chloride penetration in cement based materials. The general approach used is to solve the Nernst-Planck equation numerically for two physical ideal states that define the possible conditions under which chlorides will move through concrete. These conditions are voltage control and current control.

The first condition called “voltage control” is defined by a concrete sample placed between two electrodes that apply a constant potential difference between them. Under this condition a migration test like the ASTM C1202 [1] or NT-492 [2] can be simulated. The flow of any species present in the pore solution or in any external cells is defined according to the Nernst-Planck equation (1). In order to keep the charge neutrality throughout the sample at all times for all the ions together the term for the electrical field is distorted in each position and checked to ensure that neutrality is maintained.

$$J_i = D_i \frac{\partial c_i}{\partial x} + \frac{z_i F}{RT} D_i c_i \frac{\partial E}{\partial x} \quad \text{Equation 1}$$

In equation 1  $c_i$  is the ionic concentration of species  $i$  in the pore fluid;  $x$  the distance;  $z_i$  the electrical charge of species  $i$ ;  $F$  the Faraday constant;  $E$  is the electrical potential;  $dE/dx$  the electrical field;  $J_i$  is the flux of species  $i$ ;  $D_i$  is the diffusion coefficient of species  $i$ ;  $R$  is the gas constant; and  $T$  is absolute temperature. The electrical field  $dE/dx$  is affected by the neutrality condition is a function of the constant external applied voltage ( $\varphi$ ) and the internal voltage generated by the differences of mobility of the multispecies system ( $E_p$ ).

$$\frac{\partial E}{\partial x} = \frac{\varphi}{x} - \frac{\partial E_p}{\partial x} \quad \text{Equation 2}$$

That internal voltage is known as the membrane potential voltage [3] and physically it accounts macroscopically for all the complex phenomena involved in the pore solution (e.g. the ionic exchange and the electrical double layer). It is responsible for the non-linear behaviour of the voltage during a migration test. Microscopically the electrical field due to the membrane potential can be expressed according to the equation 3 [4].

$$\frac{\partial E_p}{\partial x} = \frac{RT}{F} \frac{\sum_i z_i D_i \frac{\partial c_i}{\partial x}}{\sum_i z_i^2 D_i c_i} \quad \text{Equation 3}$$

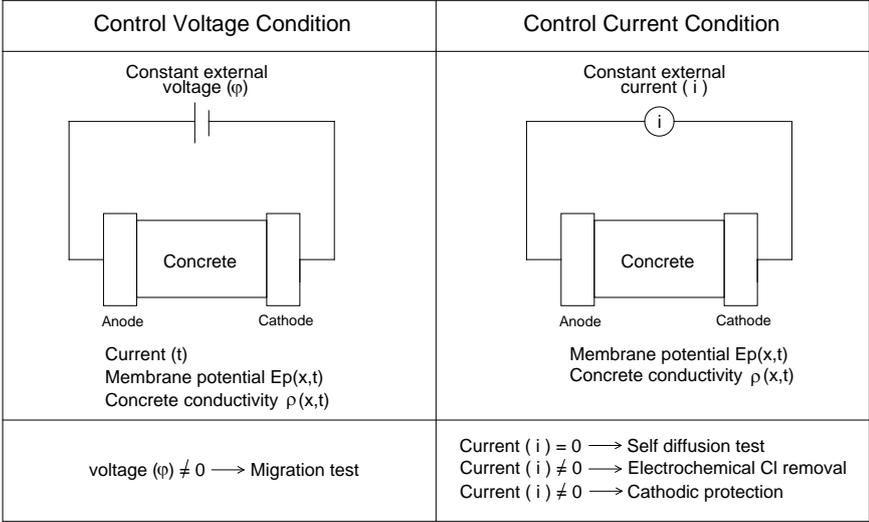
Macroscopically the membrane potential is found with the following procedure. Faraday’s law allows calculating the current passed ( $i_i$ ) for each ion (equation 4); in addition, due to Kirchhoff’s first law, for any time, the total current density that comes to a certain point must be equal to the current density that comes out of it. This means that the voltage needs to be adjusted in each point into the sample in order to ensure this condition [5].

$$i_i = -z_i F J_i A \quad \text{Equation 4}$$

The second condition is called “current control”, it makes reference to a condition similar to voltage control, but to the sample between two electrodes is subject to constant electrical current. For this condition, when the current is zero the phenomenon of normal diffusion with

no applied potential can be simulated. It is of note that when chloride ions are permitted to diffuse through concrete the system acts like a dry-cell battery and a voltage is developed. Some previous authors (ref) have modelled chloride diffusion by simply integrating Fick's law and using a diffusion coefficient for chloride ions. The true situation is, however, far more complex because the voltage that is developed will inhibit further transport unless it is dissipated by further ionic transport. This further transport may be negative ions (such as OH-) moving in the opposite direction to the Cl- or positive ions (such as Na+) moving with them and may be the determining factor for the rate of transport of the Cl-. This cannot be modelled with a voltage control algorithm set to zero applied voltage because this implies that the two ends of the sample are short-circuited. Figure 1 shows this condition for a typical sample in an ASTM C1202 test and it may be seen that current flows. Thus a new algorithm is being developed in which the system is controlled by a constant current.

If the new algorithm is used with a non-zero current the phenomena of either cathodic protection or electrochemical chloride removal can be modelled. For this condition the physical equations used are the same used previously, however, in this approach, in addition to keep the charge neutrality throughout the sample at all times for all the ions together is necessary to keep the current density constant during all the time. That new condition makes the procedure to calculate the membrane potential slightly different to the one presented previously. Figure 1 shows a schematic representation of the conditions used.



[Voltage (t)]

Figure 1 Voltage and current conditions

The voltage control model simulates a standard electrical migration test. As result, it gives the total transient electrical current, the electrical membrane potential and the ionic concentrations. As inputs, it requires the external conditions of the test and the transport related properties. Theoretically, this approach, or any similar one, gives a better understanding of the complex phenomena involved. But in a practical situation its application is limited because of the difficulties found in the determination of all the transport properties. The accurate determination of the transport related properties, especially the coefficients of

diffusion of all the species in concrete, is not easy., However, the electrical current and the electrical membrane potential can be measured experimentally.

In order to give an alternative approach to finding the transport related properties of concrete, this paper reports on a computer model based on the optimization of the voltage controlled condition. The optimization technique used was an artificial neural network (ANN) which was trained running the model a number of times and using the results as a training database. After the training process the transient current and a new test developed to measure the transient membrane potential were used to calculate the diffusion coefficients for all the ions involved. The model was applied to blended concrete mixes of Portland cement (OPC), ground blast furnace slag (GGBS), and pulverised fuel ash (PFA), for which the electrical current and the membrane potential were obtained experimentally.

## **2. MODELLING**

### **2.1. Artificial Neural Networks**

An Artificial Neural Networks (ANNs) are artificial intelligence techniques used as information processing systems, capable of learning complex cause and effect relationships between input and output data [6]. They are highly nonlinear, and can capture complex interactions among input and output variables. Like in human beings, in an ANN a neuron is connected to other neurons through links that produce a stimulus to the entry and exit as a response, in addition, they have the ability to communicate among them. A neural network has a finite number of neurons distributed in the input layer, which represents the input data, an output layer, which computes the neural networks output, and one or more intermediary layers called hidden layers, which generate the relationships between layers of entry and exit.

A neural network is trained to develop a particular task or function to adjust the intensity with which the neurons are interconnected. The back-propagation algorithm is the most used in civil engineering applications. Initially in each connection between neurons is assigned a weight, a value that is fitted during the back propagation learning process. Commonly a neural network is trained or adjusted in a way that the input variables correspond with an expected output. This situation is shown in Figure 1; the network is trained by adjusting the weights through the comparison between the outputs (values predicted by the model) and the target values.

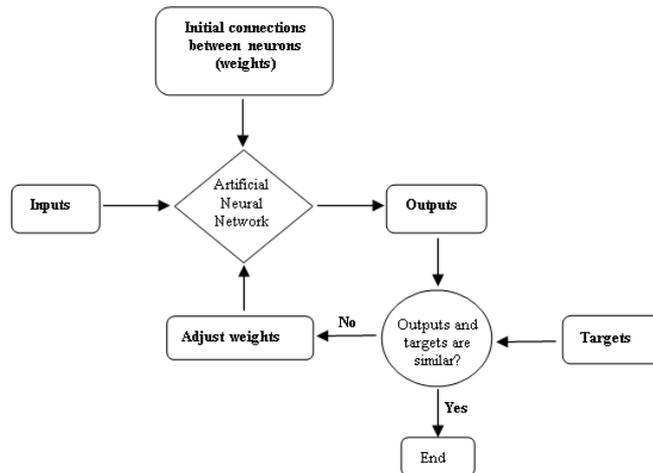


Figure 2 Back-propagation training of the neural network

## 2.2. Computer Model

The electro-diffusion numerical routine was used for calculating the transient current passed and the mid point membrane potential during a migration tests. However, as the constitutive transport properties were unknown, a neural network algorithm was trained to optimize them. As a result, with the optimization process, the transport properties of a concrete sample could be determined when the current and the mid-point membrane potential were measured during a migration test. Figure 5 shows a conceptual diagram of the model

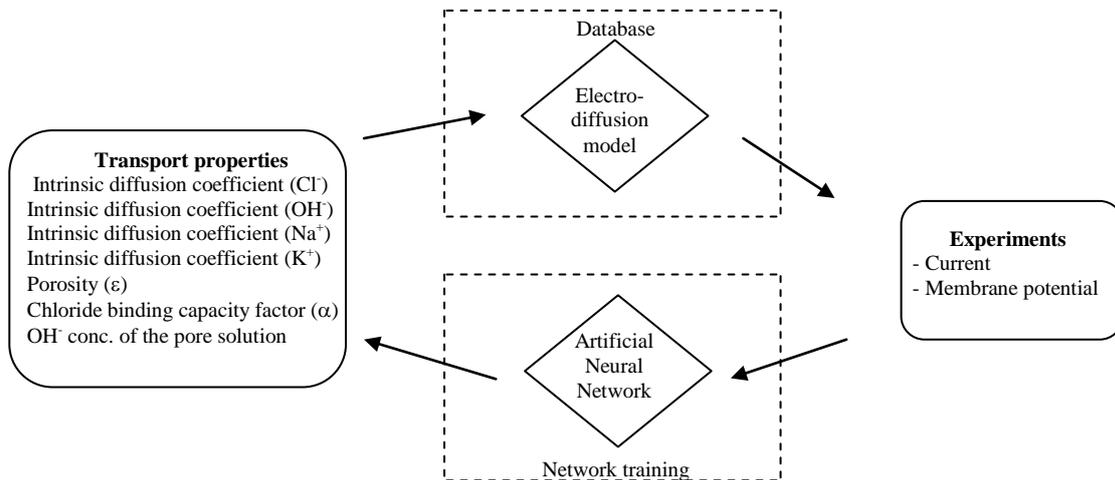


Figure 3 Conceptual diagram integrated model

The optimization model used a feed-forward back propagation-network with a multilayer architecture. Six neurons define the input layer, they correspond to values of the current and the mid point membrane potential in the sample at different times. A middle hidden layer has

3 neurons, and the output layer output has 7 neurons corresponding to the intrinsic diffusion coefficients of Cl, OH, Na and K, the porosity, the hydroxide concentration in the pore solution at the start of the test, and the binding capacity factor for chloride ions. The neural network model was constructed using the neural network tool box of Matlab<sup>TM</sup> [6].

With the current and the mid point membrane experimentally measured the transport properties were found by using the trained neural network assuming the following conditions: (i) although it has been proved experimentally that non linear isotherms describes the absorption phenomena most accurately, the binding chloride capacity calculation in the model used a linear isotherm. The ratio chloride intrinsic diffusion ( $D_{Cl}$ ) to apparent diffusion coefficient ( $D_{app-cl}$ ) is equal to the ratio binding factor capacity ( $\alpha$ ) to porosity ( $\varepsilon$ )

$$\frac{\alpha}{\varepsilon} = \frac{D_{Cl}}{D_{app-cl}} \quad \text{Equation 5}$$

(ii) At the start of the test the chemical pore solution was assumed to be composed of the ions  $OH^-$ ,  $K^+$ , and  $Na^+$ , and in order to keep the electroneutrality it was assumed that the concentration of hydroxyl ions was equilibrated with a proportion of 33% of sodium and 66% of potassium.

### 3. EXPERIMENTS

#### 3.1. Current and membrane potential in the ASTM C1202 test

The procedure used to measure the electrical current was the standard ASTM C1202 test. In this, a steady external electrical potential of 60 volts D.C was applied to a sample of concrete of 50 mm thick and 100 mm diameter . for 6 hours. The Anode and cathode were filled with 0.30 N sodium hydroxide and 3.0% sodium chloride solutions respectively. The samples were prepared for the test in conformity with the standard.

In addition to the measurements in the standard test a new electrochemical measurement was carried out. A salt bridge was added in the middle point of the sample to check the voltage distribution. A hole of 4 mm diameter and 6-9 mm deep was drilled at that point. The salt bridge used was a solution of 0.1 M potassium chloride (KCl) in order to avoid any junction potential at the interface of the salt solution and the pore solution. The voltage was measured using a saturate calomel electrode (SCE) relative to the cathode cell. The current through the concrete and the voltage in the mid point inside the sample were measured continuously every 10 seconds with a data logger. The membrane potential was calculated by subtracting the value of the voltage measured from the initial value measured at the start of the test and the value of voltage measured at any time in the midpoint position.

$$\Delta V = V_{Ti} - V_0 \quad \text{Equation 6}$$

$\Delta V$  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. A more detailed description of the experiment can be found in reference [3].

### 3.2 Materials

Concrete samples of OPC blended with GGBS and PFA with a replacement proportion of 50% and 30% respectively were mixed. Table 1 shows the mix designs and the nomenclature used in this paper. All the migration tests were carried out on samples around 100 days old which were kept in a controlled humidity and temperature room at [give RH and T]until testing.

Mix	w/b	%			Unit content: kg/m <sup>3</sup>					
		OPC %	PFA %	GGBS %	OPC [Kg]	PFA [Kg]	GGBS [Kg]	Fine agg. [Kg]	Coarse agg. [Kg]	Binder [Kg]
OPC	0.49	100	0	0	394	0	0	692	988	394
30%PFA	0.49	70	30	0	276	118	0	684	977	394
50%GGBS	0.49	50	0	50	197	0	197	690	985	394

Table1 Concrete mix design

### 4. RESULTS AND DISCUSSION

The results of the electrochemical tests for all the mixes are showed in figure 4. Each graph shows the transient current measured according the ASTM C1202 and the membrane potential at the mid point of the sample. For the graphs of membrane potential the noise found experimentally was removed with a commercial curve fitting software [7].

The trained neural network was fed with the experimentall measured transient current and the mid point voltage, and the transport related properties were calculated. The coefficients of diffusion obtained are shown in figure 5 for all the mixes and all the ions considered in this research. For the hydroxide, sodium, and potassium ions the intrinsic coefficients are presented, and for chlorides the apparent coefficients obtained according to equation 5 are shown.

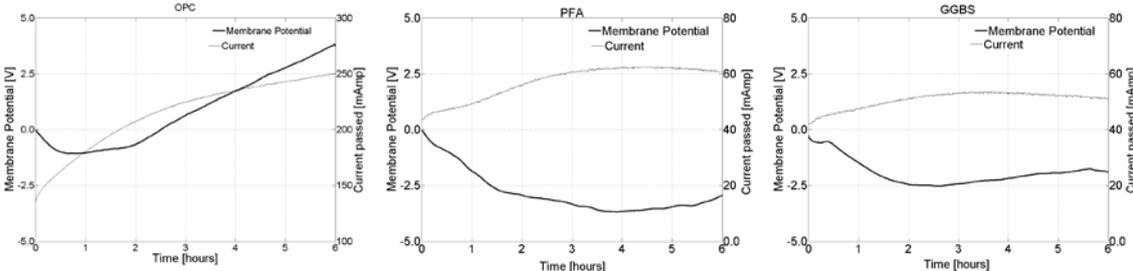


Figure 4 Membrane potential and current measured [can you show the modelled curves as well?]

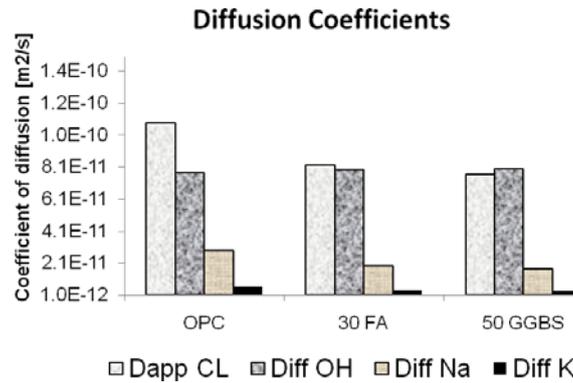


Figure 5 Coefficients of diffusion for all the species

In the same way, the porosity, the chloride binding capacity, and the initial concentration of hydroxide were calculated with the computer model at the start of the migration test. As was expected, the addition of mineral admixtures decreases the porosity, increases the capacity factor, and decreases the alkalinity of the pore solution.

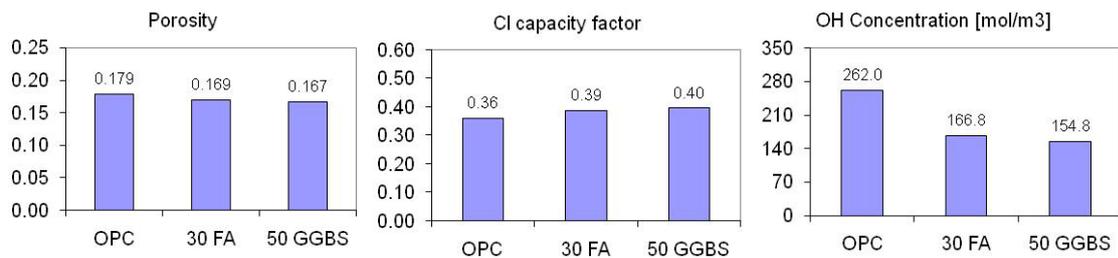


Figure 6 Porosity, capacity factor and OH<sup>-</sup> concentration estimated

## 5. CONCLUSIONS

- concreteA computer modelling system has been developed by combining an electrochemical algorithm which uses the classical equations with an optimizing neural network algorithm. The model has been used successfully in combination with a electrochemical test.
- The calculated properties will be used as inputs to simulate the penetration of chloride under a self diffusion conditions using the condition known as current control (zero current)

## 6. Acknowledgements

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

## 7. Bibliography

1. ASTM-C1202, *Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration*. 2005.
2. NTBUILD-492, *NORDTEST METHOD: CONCRETE, MORTAR AND CEMENT-BASED REPAIR MATERIALS: CHLORIDE MIGRATION COEFFICIENT FROM NON-STEADY-STATE MIGRATION EXPERIMENTS*. 1999.
3. Lizarazo-Marriaga, J. and P. Claisse, *Effect of the non-linear membrane potential on the migration of ionic species in concrete*. *Electrochimica Acta*, 2008. doi:10.1016/j.electacta.2008.11.031.
4. Lorente, S., et al., *The single-valued diffusion coefficient for ionic diffusion through porous media*. *J. Appl. Phys.*, 2007. **101**(024907).
5. Claisse, P.A. and T.W. Beresford, *Obtaining More From the Electrical Chloride Test*. ACI - SP170-57, 1997. **170**.
6. Demuth, H., M. Beale, and M. Hagan, *Neural Network Toolbox™ 6 User's Guide*, ed. Matlab. 2008.
7. The MathWorks, I., *Curve Fitting Toolbox - For Use with MATLAB*. 2001.