

## **Applicability of Traditional Electrical Techniques on Chloride Resistance Assessment of GGBS Concrete**

**Juan Lizarazo-Marriaga<sup>1,2</sup>, Peter Claisse<sup>2</sup>, and Eshmaiel Ganjian<sup>2</sup>**

<sup>1</sup>*Universidad Nacional de Colombia, Ciudad Universitaria Bogotá, E-mail <[jmlizarazom@unal.edu.co](mailto:jmlizarazom@unal.edu.co)>*

<sup>2</sup>*Coventry University, University CV1 5FB, UK, E-mail <[p.claisse@coventry.ac.uk](mailto:p.claisse@coventry.ac.uk)>, <[E.Ganjian@coventry.ac.uk](mailto:E.Ganjian@coventry.ac.uk)>*

### **ABSTRACT**

In this paper the reliability of the electrical ASTM C1202 RCPT and resistivity tests was studied to assess the chloride resistance of GGBS mixtures with different levels of replacement. In order to achieve this, a computational model was used to investigate the influence of the level of GGBS replacement on the electrical assessment of the chloride related transport properties. Results of the experiments and the simulations showed that the resistivity and the total electric charge passed can be used as indirect measures of the chloride resistance in OPC-GGBS mixes.

### **INTRODUCTION**

Slag is a by-product of the smelting process, it is a foundry residue. Depending on which metals are being produced, slags will have different mineralogical properties. Production of Iron, steel, copper, lead, and aluminium dominate the metallurgical industry, generating vast volumes of slag. Depending on its chemical and physical properties a slag could be used (a) in the construction industry as aggregate in granular bases, asphalt mixes, cement replacement and concrete mixes, or (b) in bulk applications such as embankments and bulk fills. The utilization of slags as cement raw material or as replacement in blended concretes has been extensively studied for reasons such as the environmental benefits, the potential cementitious or pozzolanic properties and the high cost of the Portland cement. Worldwide, the most commonly used slag is ground granulated blast Furnace slag (GGBS) - from the iron industry.

Although the mechanical properties and the high chloride resistance of GGBS blended concretes are well known, the level of replacement of the mineral admixture used can have an important effect on some transport properties, especially, on the porosity, the binding capacity and the conductivity of the pore solution:

- It has been reported by Geiseler, Kollo and Lang [1992] that the capillary porosity, for pores with radius more than 30 nanometres, decreases proportionally the increase in the GGBS amount.

- Chloride binding can be explained either by chemical or physical interactions between chlorides and the hydration products of concrete. Chemical binding forms compounds like Friedel's salt ( $\text{Ca}_3\text{Al}_2\text{O}_6\text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ ), where an increase in the amount of  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$  in the cement paste determines an increase in its capacity of binding. Mineral admixtures like GGBS increase the chloride binding due to the high content of aluminate hydrates [Yuan et al., 2009].
- The use of mineral and chemical admixtures changes the composition of the pore solution of concrete. Different studies have shown how the use of silica fume, GGBS, metakaoline, fly ash [Page and Vennesland 1983] and corrosion inhibitors or accelerators [Corbo and Farzam 1989] have a strong effect on the chemical composition and conductivity of the pore solution. The addition of supplementary cement materials results in a moderate reduction of ionic concentration and of the pH.

Although the chloride resistance of concrete mixes can be assessed using long term experiments, these are very expensive and time consuming (months). In contrast, accelerated electrical tests need just short periods of time (hours or minutes). Two of those traditional electrical tests used frequently to assess the chloride resistance of concrete are the ASTM C1202 "Rapid chloride penetrability test" [ASTM-C1202 2005] and the electrical resistivity [Hossain 2005]. Even though there are no doubts about the good correlation between the concrete transport properties and the charge or resistivity measured for ordinary Portland cement (OPC) mixes, there is still a lack of understanding on the effect of those electrical parameters on the chloride transport properties of GGBS mixes with different levels of replacement.

Taking into account the above statements, the main objective of this paper was to study the reliability of the RCPT and resistivity tests to assess correctly the chloride resistance of GGBS mixtures with different levels of replacement. In order to achieve this, a numerical model, composed of a physical multi-species approach and a neural network optimization approach was used to investigate the influence of the level of GGBS replacement on the assessment of the chloride related transport properties.

## **MODELLING**

A computational model developed previously was used to calculate the chloride transport properties of the GGBS concrete mixes from an electrochemical test [Lizarazo-Marriaga and Claisse 2009a]. The model was composed of a physical approach and an optimization technique. The physical algorithm used a finite difference scheme to simulate the RCPT test solving the Nernst-Planck equation. This calculates the ionic fluxes of all the species involved and keeps charge neutrality by modelling changes to the voltage distribution through the generation of an additional voltage called membrane potential [Claisse 2009]. The optimization approach used a feed-forward back propagation-network with a multilayer architecture. For this, the inputs are the experimental results of transient current and membrane potential of an RCPT test [Lizarazo-Marriaga and Claisse 2009b] and the outputs are the transport properties, such as the intrinsic diffusion coefficients, the porosity, the hydroxide concentration in the pore solution at the start of the test, and the binding capacity factor

In the model the following assumptions were proposed:

- (i) The binding chloride capacity was defined using a linear isotherm and binding was allowed only for chlorides. For other species ( $\text{OH}^-$ ,  $\text{K}^+$ , and  $\text{Na}^+$ ) binding was not considered.
- (ii) The intrinsic coefficient ( $D_{\text{int}}$ ) defines the transport of matter when the flux is calculated per unit cross-sectional area of the pores and the concentration in the free liquid. In contrast, the apparent diffusion coefficient ( $D_{\text{app}}$ ) defines the transport of any ion when the flux is calculated per unit area of the porous material and the average concentration in the material.
- (iii) The ratio intrinsic diffusion ( $D_{\text{int}}$ ) to apparent diffusion coefficient ( $D_{\text{app}}$ ) is equal to the ratio binding factor capacity ( $\alpha$ ) to porosity ( $\varepsilon$ )

$$\frac{\alpha}{\varepsilon} = \frac{D_{\text{Cl}}}{D_{\text{app-cl}}} \quad (1)$$

- (iv) At the start of the test the chemical pore solution was composed only of  $\text{OH}^-$ ,  $\text{K}^+$ , and  $\text{Na}^+$ . It was assumed that the concentration of hydroxyl ions was equilibrated with a proportion of 33% of sodium and 66% of potassium.

In this paper a full discussion about the model and the electrochemical method used to calculate the transport properties is not given; however, in the references given above, there is a complete description of the numerical and experimental techniques used.

## EXPERIMENTS

### Current, charge and membrane potential

The electrical current was measured according to the standard ASTM C1202. In this, an external voltage of 60 volts D.C was applied to a sample of concrete for 6 hours. The sample was in contact with a solution of sodium hydroxide in the anode and with a solution of sodium chloride in the cathode. The samples were water saturated before the test according to the standard.

In addition to the standard measurements, the voltage evolution was monitored in the mid point of the sample. For this, a salt bridge with a solution of potassium chloride (KCl) was used. The voltage was measured using a saturated calomel electrode (SCE) relative to the cathode cell. The membrane potential was calculated by subtracting the value of the voltage measured at the start of the test from the value of voltage measured at any time in the midpoint position [Lizarazo-Marriaga and Claisse 2009b].

### Resistivity

The A.C. resistivity was measured on fully saturated samples before the RCPT tests using two probes. The electrodes were the same cells employed during the migration tests including the

same solutions of the reservoirs. For this, an electrical A.C. signal generator and calibrated resistances were used. The voltage applied was between 6 and 8 Volts.

## MATERIALS

### Materials used

The materials used in this research were obtained from different sources. A summary of them is presented below.

Two different brands (A and B) of commercial Ordinary Portland cement (OPC) classified as CEM-1 according BS EN 197-1 “Composition, specifications and conformity criteria for common cements” and composed of 95-100% clinker were used. Those were free of admixtures except the gypsum acting as a retarder. The Ground Granulated blast furnace slag (GGBS) was obtained from Civil and Marine, a part of Hanson UK. The material was marketed under the standard BS 6699 “Specification for ground granulated blast furnace slag for use with Portland cement”.

Sand with a calculated fineness modulus of 3.3 and a dry density of 2660 kg/m<sup>3</sup> was used. Coarse aggregate from a quarry with a mixed surface texture of both rounded smooth and angular rough particles and a dry density of 2650 kg/m<sup>3</sup> was used (5-13 mm).

### Mix design

Samples of OPC and GGBS were cast using different levels of GGBS replacement (0, 10 30, 50 and 60%). The mixes were designed using two water-binder ratios (0.40 and 0.50) and were cured in wet conditions for all cases for more than 90 days.

**Table 1. Mix Design**

#	Mix	Prop.	W/B	Binder [kg/m <sup>3</sup> ]			Water	Sand	Gravel
				OPC	GGBS	Total	Kg/m <sup>3</sup>	Kg/m <sup>3</sup>	Kg/m <sup>3</sup>
1	O5-A	100%OPC	0.49	394	0	394	193	692	988
2	OG5-10-A	90%OPC+10%GGBS	0.49	355	39	394	193	691	987
3	OG5-30-A	70%OPC+30%GGBS	0.49	276	118	394	193	690	986
4	OG5-50-A	50%OPC+50%GGBS	0.49	197	197	394	193	690	985
5	O4-B	100%OPC	0.4	400	0	400	160	705	1058
6	O5-B	100%OPC	0.5	400	0	400	200	664	995
7	OG4-30-B	70%OPC+30%GGBS	0.4	280	120	400	160	704	1055
8	OG4-50-B	50%OPC+50%GGBS	0.4	200	200	400	160	702	1054
9	OG5-30-B	70%OPC+30%GGBS	0.5	280	120	400	200	662	993
10	OG5-50-B	50%OPC+50%GGBS	0.5	200	200	400	200	661	991

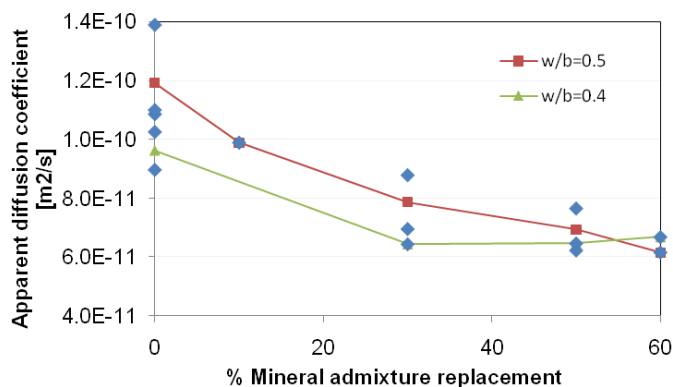
## RESULTS AND DISCUSSION

For the GGBS mixes cast the transient current and the transient membrane potential were measured during the ASTM C1202 electrochemical test, additionally, the total charge and measured the AC electrical resistivity were measured for all the mixes. The transport related properties were obtained from the experimental results using the neural network optimization model.

All the migration tests carried out were in non-steady state conditions because of the characteristics of the experiments, in which there were small volume external cells, a high external voltage, and a short duration. Although in some mixes it was possible that the chlorides reached the anode (thus giving a uniform condition through the sample), the depletion of the external cells ensured that a steady state condition was never achieved. Therefore, the estimated intrinsic diffusion coefficients were for non steady state conditions.

### Simulation of transport related properties

For the OPC-GGBS mixes the apparent chloride diffusion coefficients were found using equation 1, which establishes the relationship between the apparent and intrinsic chloride diffusion coefficients. Figure 1 shows the effects of GGBS on the apparent Cl diffusion coefficient. An increase in GGBS produces a reduction in the diffusion coefficient. The calculated apparent diffusion coefficients obtained were relatively high compared with some reported in the literature. Usually, for a concrete of good quality, a chloride diffusion coefficient in the order of  $10\text{-}12\text{ m}^2/\text{s}$  is expected. However, these differences can be explained by the fact that the diffusion coefficients obtained in this research apply to a multi-species system coupled through the membrane potential, rather than of those obtained in experiments reported in literature where ions are physically affected by the ionic exchange among species, but the coefficients are calculated with equations that account for only chloride diffusion in isolation and no ionic interaction.

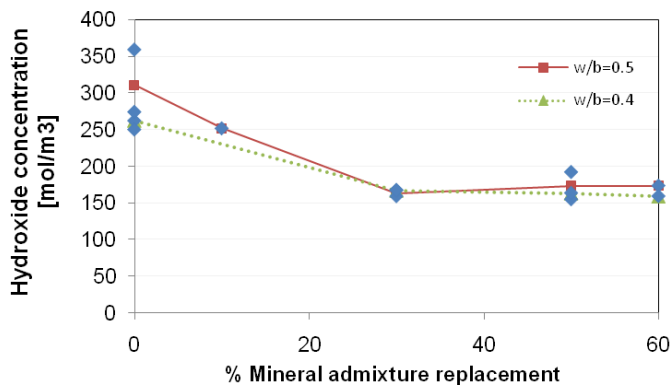


**Fig. 1. Simulated Effects of GGBS on the Cl Apparent Diffusion Coefficient**

Figure 2 shows the influence of the proportion of GGBS on the  $\text{OH}^-$  concentration at the beginning of the test. The individual points show the data obtained from the experiment and the resulting average is shown as continuous line for each water to binder ratio.

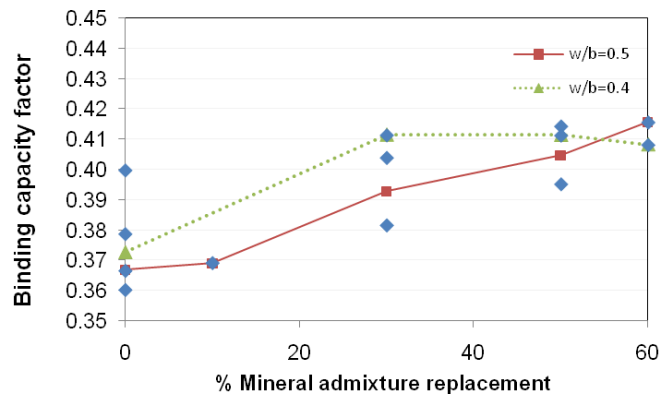
For the OPC samples with water binder ratio of 0.5, for example, an average value of  $311 \text{ mol/m}^3$  was obtained for hydroxyl concentration. This corresponds, according to the model assumptions stated above, to  $102 \text{ mol/m}^3$  of sodium and  $189 \text{ mol/m}^3$  of potassium in order to maintain the initial electro-neutrality of the system (units in mol per cubic meter of pore solution). As was expected, with the increase of the amount of the mineral admixture, a reduction was found in the initial hydroxide composition of the pore solution. This was previously reported by Page and Vennesland [1983]. The calculated hydroxide reduction of the solution into the pores for the 30% GGBS blended concrete was around 40% with respect to the OPC. Above 30% of replacement, there was no further reduction in the hydroxide ion concentration.

From the figure it can be seen that the water binder ratio does not have an important influence on the hydroxide concentration for GGBS blended mixtures, while for unblended mixes (OPC) the calculated initial chemical content of the pore solution seems to increase with an increase in the water binder ratio. This can be attributed to the higher amount of water, which causes a decrease in the ability of the hydration products to fix alkali metals.



**Fig. 2. Simulated Effects of GGBS Replacements on Hydroxide Composition**

The calculated chloride binding capacity factor is shown in figure 3. It was found that it tends to increase with an increase in the amount of mineral admixture; similar results were found by Dhir, El-Mohr and Dyer [1996]. The greatest chloride capacity factor was found in mixes of 60% GGBS for 0.5 w/b and in mixes of 30% GGBS for 0.4 w/b.

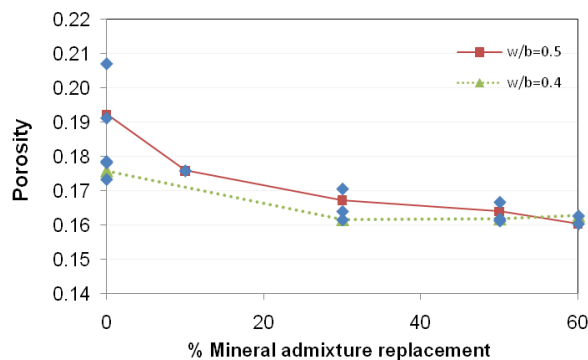


**Fig. 3. Simulated Effects of GGBS on the Chloride Binding Capacity**

From the integrated model, the calculated porosity was also found. There was a reduction in the porosity with an increase in the amount of admixture and the beneficial effect of GGBS was greatest using 60% of GGBS. Figure 4 shows the variation of the calculated open porosity for different percentages of admixture. As was expected, the porosity increases with an increase of the water binder ratio, especially for low levels of GGBS replacement.

**Effect of slag replacement on measured charge and resistivity**

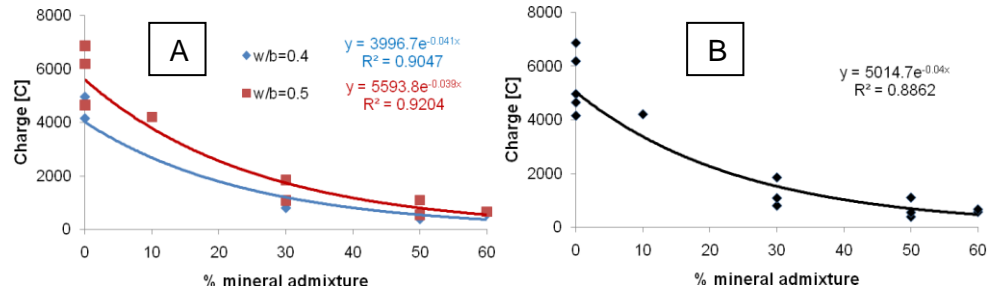
The resistivity and charge passed are good indicators of the chloride penetration for samples containing only OPC. However, the electrical properties of concrete are related, in addition to their diffusion coefficients, to the pore solution composition. In that way, using GGBS as mineral admixture to replace OPC produces changes in the electrical properties of the material, and those changes could be related with variations on the chemical composition of the pore solution rather than with the concrete resistance to chloride penetration.



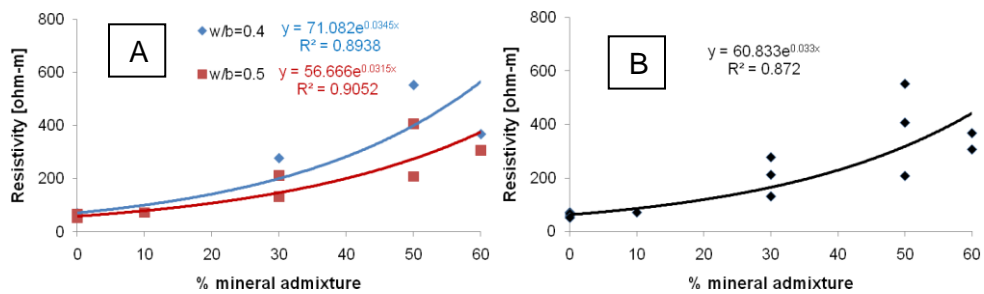
**Fig. 4. Simulated Effects of GGBS on the Porosity**

The effect of GGBS replacement on the charge passed and resistivity is shown in figures 5 and 6 respectively. In figures “A” the relationships for samples of different water binder ratio are

shown, and in figures “B” a general relationship obtained using all the data available are shown. The equations that best fit the experimental results are shown in the figures.



**Fig. 5. Effect of GGBS Replacement on the Charge Passed**

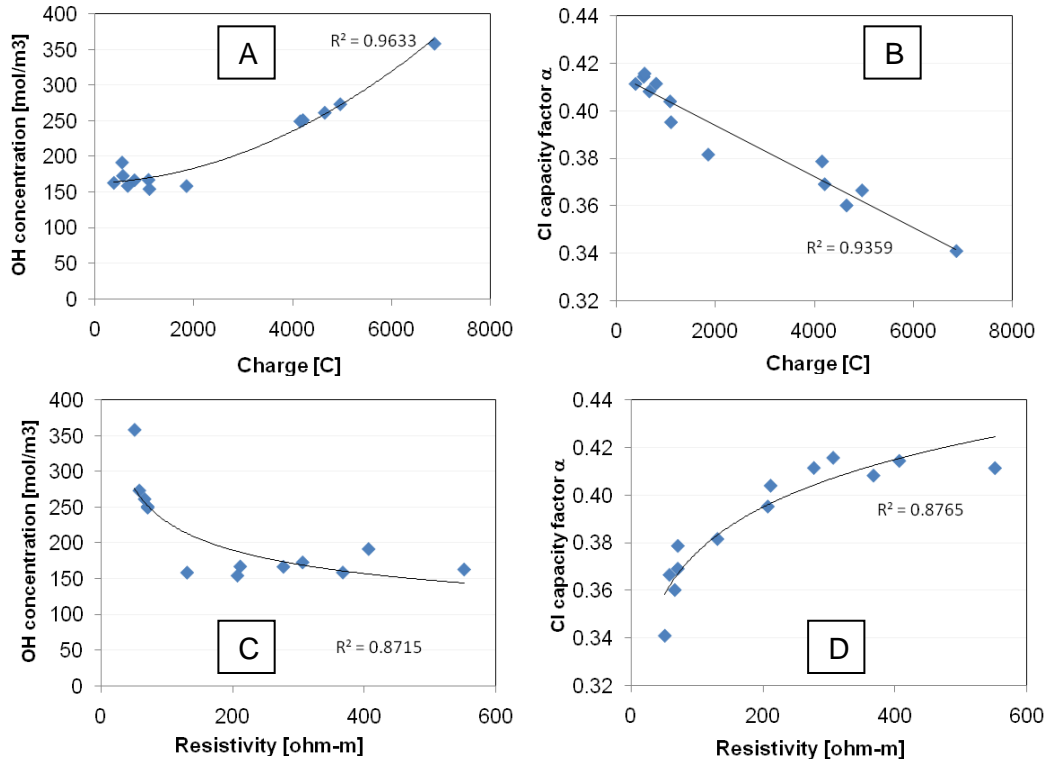


**Fig. 6. Effect of GGBS Replacements on the Resistivity**

**Correlation of the estimated properties with the charge and resistivity**

The effects of the resistivity and charge passed on the alkalinity of the pore solution, defined as a function of the OH<sup>-</sup> initial concentration, and the chloride capacity factor are shown in figure 7. As was expected, a good correlation was found between both electrical tests and the hydroxide concentration calculated with the computational model (figures A and C). The conductivity of a concrete sample is strongly related with the conductivity of the pore solution as was pointed out by Shi, Stegemann and Caldwell [1998]. In the same way, a good relationship was found between the measured electrical properties and the chloride capacity factor (figures B and D). This last observation has great importance because for samples OPC-GGBS, the binding capacity is one of the key factors which dominates the penetration of chlorides. If the electrical tests are, at the same time, dependent on the pore solution concentration and the chloride capacity factor, it can be argued that when the tests are applied to OPC-GGBS mixes, the conductivity of pore solution is measured, but equally the chloride resistance of chlorides is measured.





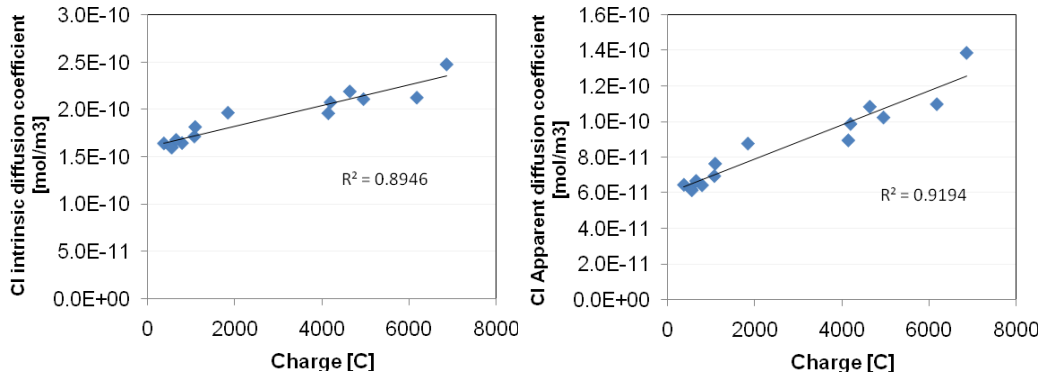
**Fig. 7. Effects of Charge and Resistivity on the Chloride Capacity Factor and Initial Alkalinity**

The relationship between the charge in Coulombs obtained from the standard ASTM C1202 test and the calculated intrinsic (left) and apparent (right) diffusion coefficients is shown in figure 8. The link between both coefficients was defined by equation 1. The reason why both coefficients are presented is because the intrinsic diffusion coefficient relates to the diffusivity of the pore solution rather than the diffusivity of the porous medium. It does not include the microstructure properties of concrete (i.e. porosity, tortuosity, or binding capacity). However the apparent diffusion coefficient  $D_{app}$ , takes account of the porosity, tortuosity, and the binding capacity of the concrete matrix.

From the figures can be seen that the charge-chloride diffusion coefficient relationship for GGBS had an acceptable correlation with determination coefficients of  $R^2=0.895$  and  $0.919$ . According to this, equations 2 and 3 define that relationship and can be used as a tool to estimate the diffusion coefficients in  $[m^2/s]$  from the measured value of charge [in Coulombs] for GGBS mixes (GGBS replacement between 0 and 60 percent).

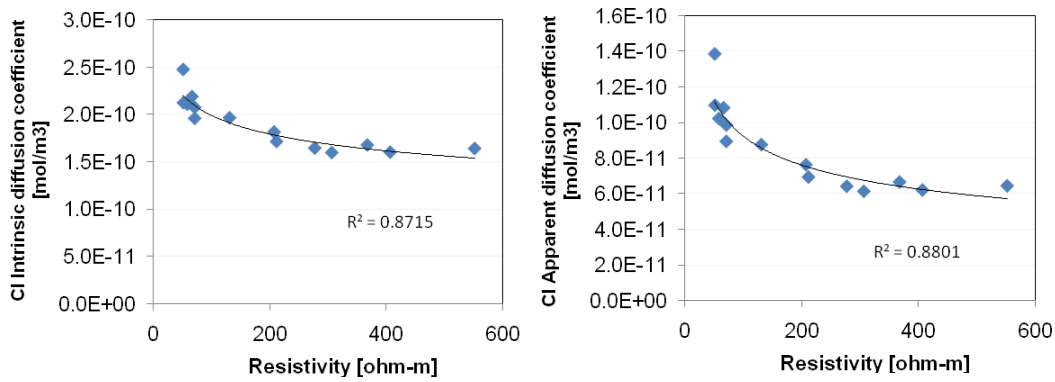
$$D_{int-GGBS} = 1 \times 10^{-14} \times Charge + 2 \times 10^{-10} \quad (2)$$

$$D_{app-GGBS} = 1 \times 10^{-14} \times Charge + 6 \times 10^{-11} \quad (3)$$



**Fig. 8. Simulated Effects of GGBS on the Cl Diffusion Coefficients**

The relationships between the electrical resistivity and the calculated chloride diffusion coefficients are shown in figure 9 and equation 4 and 5.



**Fig. 9. Simulated Effects of GGBS on the Cl Diffusion Coefficients**

$$D_{\text{int-GGBS}} = 4 \times 10^{-10} \times \text{Resistivity}^{-0.151} \quad (4)$$

$$D_{\text{int-GGBS}} = 3 \times 10^{-10} \times \text{Resistivity}^{-0.283} \quad (5)$$

## CONCLUSIONS

1. The proportion of slag used in OPC-GGBS mixes affects the measured charge and resistivity. Those relationships are non-linear, an increase in the mineral admixture corresponding to an increase in the resistivity and a decrease in the total charge passed.
2. Using Artificial Neural Networks trained on numerical simulations of the migration test yields viable results for the fundamental properties of concrete. The initial hydroxide composition of the pore solution, the chloride binding capacity, the porosity, and the diffusion coefficients for all the species involved can be obtained.

3. The low chloride penetration in GGBS blended mixtures may be attributed to many factors; however, it is believed that the binding capacity factor is the predominant one.
4. The use of the resistivity and the total electric charge passed as indirect measures of the chloride penetration is suitable in OPC-GGBS mixes. The low values of resistivity are related with the conductivity of the pore solution, but are intimately linked as well to the binding capacity and the diffusivity of chlorides. Some equations are given to correlate the diffusion coefficients with the charge and resistivity.

## ACKNOWLEDGEMENTS

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

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