

Monitoreo mediante EIS del acero embebido en un concreto de escoria activada alcalinamente expuesto a carbonatación

EIS monitoring of embedded steel in alkali activated concrete exposed to carbonation

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Resumen

En este trabajo se utilizó la técnica de espectroscopia de impedancia electroquímica (EIS) para evaluar la acción del dióxido de carbono sobre la corrosión de un acero estructural ASTM A 706 embebido en un concreto de escoria activado alcalinamente (AAS), el concreto AAS es una mezcla de escoria molida granulada, agregados finos y gruesos y solución alcalina (silicato de sodio) en la cantidad requerida para la mezcla de concreto. El estudio se realizó comparativamente con especímenes expuestos a condiciones naturales con una baja concentración de CO₂ (0,03% CO₂). La carbonatación del concreto se obtuvo de forma acelerada bajo condiciones controladas (3% CO₂, 65% de humedad relativa y 20°C de temperatura). Los datos de Impedancia fueron adquiridos en un rango de 1mHz hasta 100kHz. A las frecuencias altas se encontró la respuesta de la interfase medio de exposición-concreto y a frecuencias bajas la respuesta de la interfase correspondiente al concreto – acero. Mediante EIS se estableció la capacidad de lograr la pasivación del acero embebido en concreto AAS, en condiciones ambientales naturales y aceleradas.

Palabras Clave: AAS, carbonatación, EIS

Abstract

In this work the technique of impedance spectroscopy electrochemistry (EIS) was used to evaluate the effects of carbon dioxide on the corrosion of ASTM A 706 structural steel embedded in concrete with alkali activated slag (AAS), AAS concrete is a mixture of ground granulated slag, fine and coarse aggregates and alkaline solution (sodium silicate) in the amount required for the concrete mix. The study was conducted in comparison with specimens exposed to natural conditions with a low concentration of CO₂ (0.03% CO₂). The carbonation of the concrete was obtained through accelerated carbonation under controlled conditions (3% CO₂, 65% of relative humidity and 20°C of temperature). The data of Impedance in the middle frequency region 1mHz - 100KHz. A high frequency response was found using the interface-specific exposure and low frequency response corresponding to the specific interface – steel. EIS was used to established the ability to achieve passivation of steel embedded in AAS concrete in natural and accelerated environmental conditions.

Keywords: AAS, carbonation, EIS

1. Introduction

In the search of energy saving and minimization of natural resources consumption, the proper use of by-products and industrial waste (fly ashes, silica fume, steel industry-blast furnace slag, among others) have become relevant over the past few years, therefore, concrete industry has entered into the development and production of new alternative types of cements (Shi 1996).

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Among such materials, known as supplements or admixtures, granulated blast furnace slag (GBFS) has been successfully used as partial or total substitute for regular Portland cement among concrete mixtures, thus providing materials of higher mechanical performance and life span. GBFS employed without Portland cement has a fast hydration when mixed with an adequate activator, such as a sodium silicate solution. If GBFS is mixed with aggregates, it is able to produce a concrete developing a high mechanical strength at early ages and creates dense non-permeable concrete (Shi 1996; Fernández-Jimenez, A; Puertas, F 2003; Fernández-Jiménez A., Palomo A 2009). On the other hand, this new type of cement contributes to sustainable development thanks to a decrease of CO₂ emissions and to lower natural resources consumption (Aperador et al., 2009).

Reinforced steels embedded in concrete, produced with Portland cements and alkali activated slag (AAS), are naturally protected against corrosion due to high alkalinity hardness of this medium, specifically in the steel-matrix interface. However, protection condition may be affected by passive film deterioration due to pH drop in the reinforcement zone (carbonation) and, it may also lead to mechanical properties loss and life span reduction (Blanco et al., 2006; Song and Saraswanthy 2006; Aperador et al., 2009).

A relevant technique for the study of concrete corrosion is electrochemical impedance spectroscopy (EIS), which operates under frequency dominance field. EIS is based on the concept that a given interface can be regarded as a combination of passive elements in an electric circuit such is the case for strengths, capacitors and inductors. This technique is widely accepted for structural electrochemical studies due to the accuracy of polarization resistivity values (pR). Furthermore, it delivers fundamental information on system characteristics, although results interpretation is sometimes hard to achieve. Besides it is a technique that involves long execution times. EIS technique was first employed for corrosion assessment on steels embedded in concretes by early 90's and today it is considered as great help technique to understand the behavior of steel/concrete system (Feliu et al., 1998; Moreno et al., 2004; Bastidas et al., 2008a; Bastidas et al., 2008b).

Technical response is a diagram for imaginary absolute values against impedance resistive component forming a semicircle, where diameter is polarization resistivity and X-axis intercept point (resistive component), providing concrete strength at high frequency range. Resistivity is remarkable in the case of concrete, sometimes in $k\Omega \cdot cm$ range, therefore, it may affect the response of steel-concrete interface and deliver an erroneous reading. Consequently polarization resistivity measurement shall be made by using ohmic compensations.

The purpose of this research is to expose electrochemical properties of steel embedded in alkaline activated concrete when set under normal atmospheric and environmental conditions, with 3% of CO_2 concentration. Electrochemical impedance spectroscopy at different exposure periods, up to 1050 hrs, was conducted for AAS concretes.

2. Experimental procedure

2.1 Concrete samples and elaboration of specimens

A Colombian-Steel industry-blast furnace slag was employed as 100% cement mix having a chemical composition of 33.7 % SiO_2 , 12.8% Al_2O_3 , 45.4% CaO , 0.5% TiO_2 and 1.00 % MgO ; basicity coefficient ($CaO+MgO/SiO_2+Al_2O_3$) and quality coefficient ($CaO+MgO+Al_2O_3/SiO_2+TiO_2$) of 1.0 and 1.73, respectively. A sodium silicate solution was employed as alkaline activator with a 5% concentration of Na_2O , expressed in percentage of slag weight. The employed aggregates contain gravel of 19 mm maximum size having a specific gravity of 2.94, 1.3% absorption and; lake sand with specific surface of $2470 \text{ km}^2/\text{m}^3$ and 2.9% absorption. Concretes were elaborated from such materials with 400 kg cement mix per concrete m^3 , with a 0.4 water/cement ratio.

For electrochemical measurements, cylinders of 76.2 mm diameter per 76.2 mm height were elaborated containing a structural ASTM A 706 steel rod inside, which is placed at the specimen center; diameter of reinforced steel is 6.35mm. The arrangement can be observed in Figure 1, where the exposed steel length reaches 50mm. AAS concretes were previously cured at 90% relative humidity for 28 days from the test.

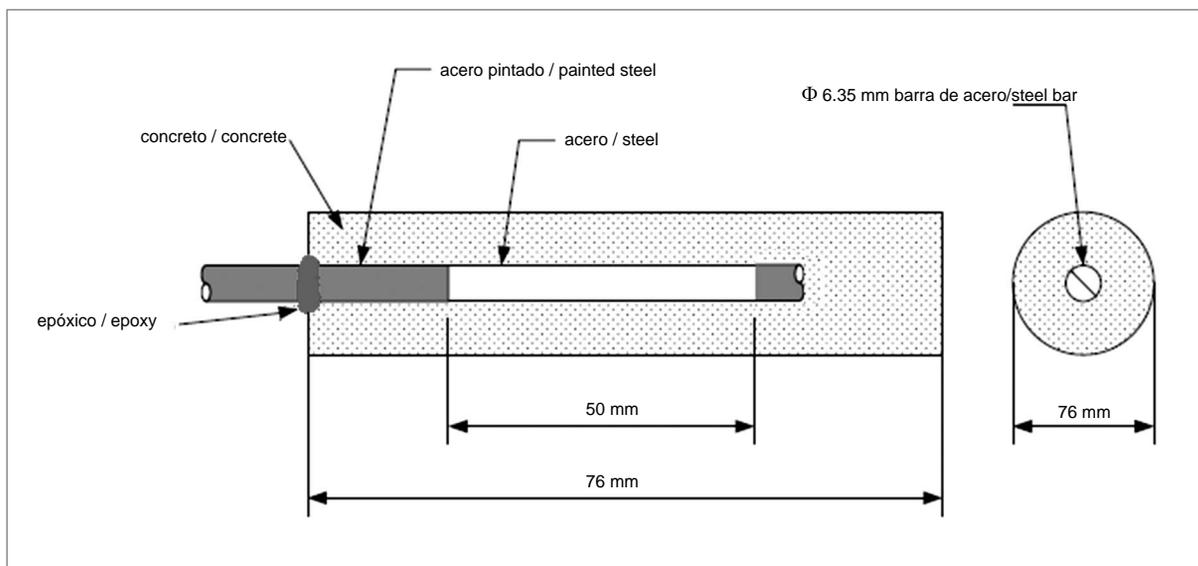


Figura 1. Esquema de la preparación de la muestra de concreto armado
 Figure 1. Arrangement of sample elaboration for reinforced concrete

The process for measuring corrosion progress due to the inclusion of carbon dioxide was conducted by means of a carbonation chamber under controlled conditions (3%CO₂, 65% relative humidity and at 20° C temperature). So as to compare results obtained by carbonation, measurements were taken from specimens exposed to environmental conditions: 68% relative humidity, 28°C and 0.03% CO₂. Compressive strength in concrete samples was evaluated at initial condition (28 curing days) and after carbonation process was concluded (Puertas et al., 2006; Moreno et al., 2004).

2.2 Electro-chemical Test

The electro-chemical characterization was made by means of a Gamry potentiostat/galvanostat, Model PCI 4 employing the electrochemical impedance spectroscopy technique, by using a cell composed by a graphite counter-electrode, an Ag/AgCl reference electrode and, as working electrode an ASTM A 706 structural steel with a exposure area of 10 cm² was used.

Electrochemical measurements were taken from AAS concretes at 0 hours = level 0, 350 hours = level 1, 700 hours = level 2 and 1050 hours = level 3 of exposure. It is noticeable that AAS specimens at 1050 hours are completely carbonated. Measurements on concretes exposed to natural environment were taken at the same exposure ages.

All electrochemical tests were conducted under distilled water solution submersion. Figure 2 depicts the test arrangement. Nyquist diagrams were obtained employing frequency scanners within a range of 100 kHz up to 0.001 Hz, by using sinusoidal wave amplitude of 10 mV.

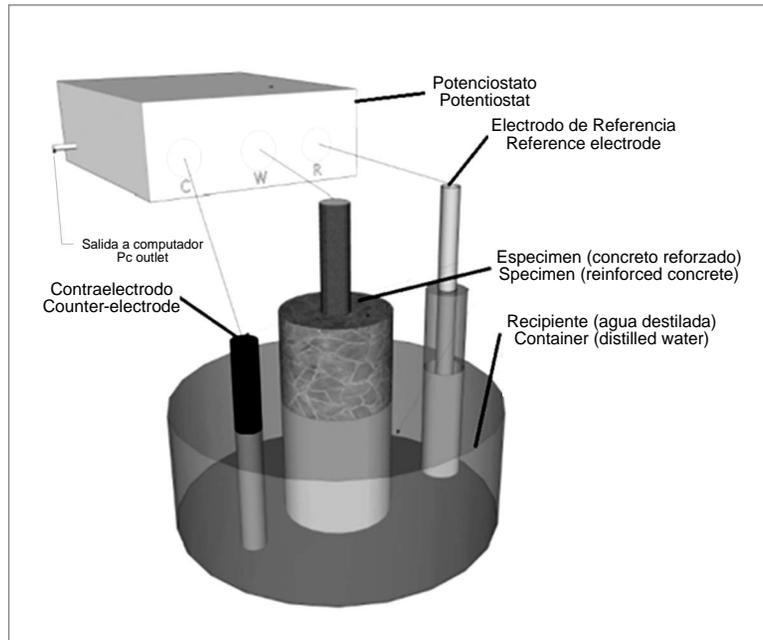


Figura 2. Montaje experimental para la realización de las medidas electroquímicas
Figure 2. Experimental arrangement for electrochemical measurements

3. Results and discussions

3.1 Determination of compressive strength on AAS concretes

Compressive strength results are shown in Figure 3, where symbols AASA and AASC represent specimens exposed to natural environment and to accelerated carbonation chamber, respectively. It can be observed that natural exposure does not affect strength; on the contrary concretes evaluated at 1050 hours and exposed to accelerated carbonation present a 30% compressive strength decrease in comparison to values at 28 curing days. It may be explained due to CO₂ attack on hydrate calcium silicate, which is responsible for mechanical properties of the material, thus agreeing with reports by other researchers (Shi 1996; Fernández-Jimenez, A; Puertas, F 2003).

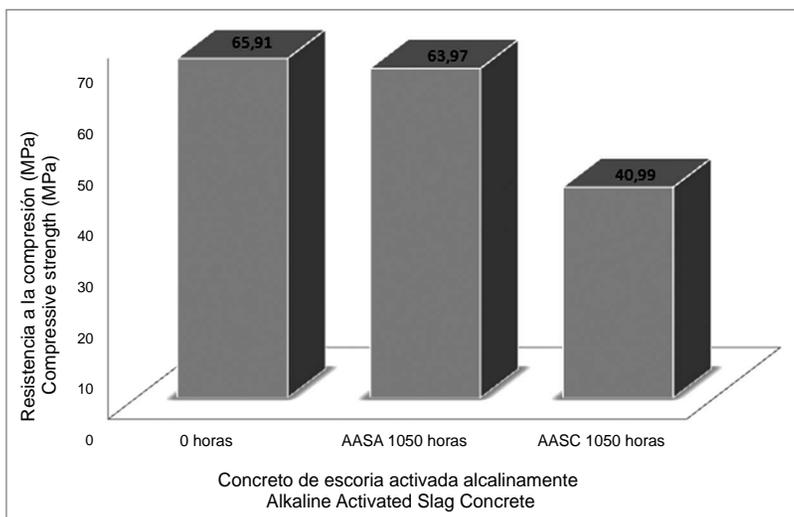


Figura 3. Resistencia mecánica del concreto AAS
 Figure 3. Mechanical Strength of AAS concrete

3.2 Electrochemical Impedance Spectroscopy (EIS) 3.2.1 Exposure in carbonation chamber

Impedance technique applied on AAS concrete delivered several physical models, depending on evaluation stage. For the case of concrete exposed to accelerated carbonation (Figure 4), it is noticeable that in first evaluated level, i.e 0 exposure hour, modified Randles model was found provided that Warburg element is present, which is the first electrochemical element introduced for description of impedance linear semi-finite diffusion, complying with the second Fick's Law.

$$\partial c / \partial t = D(\partial^2 c / \partial x^2) \quad (1)$$

As indicated in Figure 5 the introduction of a serial Warburg element with load transfer strength is explained by responses of faradaic processes taking place in the interfase. Such effect explains why stationary stage cannot be found by means of conventional techniques such as direct current, linear polarization resistance and Tafel polarization curves. They also explain observed time constants of impedance spectrums at low frequencies and the need to exceed polarization resistivity values (Montemor et al., 2003). Montemor proved that such time constant could be related with concrete humidity. The high frequency response also enables the determination of concrete resistivity.

The presence of dislocated semicircles suggests a non-ideal condenser behavior, allowing the introduction of a constant phase element (CPE), which increases determination accuracy of polarization resistivity. Obtained values, from outcomes processing on AAS 0 hours, are included in Table 1.

Figure 4 indicates electrochemical impedance spectrums of steel industry-blast furnace slag concrete alkaline activated with exposure to accelerated carbonation. The sample called AAS was evaluated at 28 curing days. In the first carbonation level, material is affected by carbonation effect, which can be proven due to the decrease of electrochemical properties in comparison to initial condition; the same behavior is reflected by carbonated samples of second and third levels. It is also observed that concrete strength value (R_{c+s}) at four different carbonation levels is quite similar, thus indicating that pores concrete resistivity (denomination for such parameter) has a constant trend, however, this value has decreased in comparison to AAs concrete at 28 curing days, which indicates that matrix quality has been altered by carbonation effect and therefore, carbonated concrete can easily lead to a corrosive process over structural steel. R_1 resistivity value, which has been related to reactions formed in cement/aggregates interface, is reduced as long as thickness of carbonated concrete increases. The same behavior is observed for the so called R_2 resistivity, where at longer carbonation period, the values of such parameters decrease. CEP1 capacitance value decreases as long as carbonation time goes by. This is explained because of the layer that had started to generate in the aggregates interfase. Contrarily CPE2 shows an increasing trend because steel passivation layer becomes vulnerable as long as carbonation reactions take place in concrete.

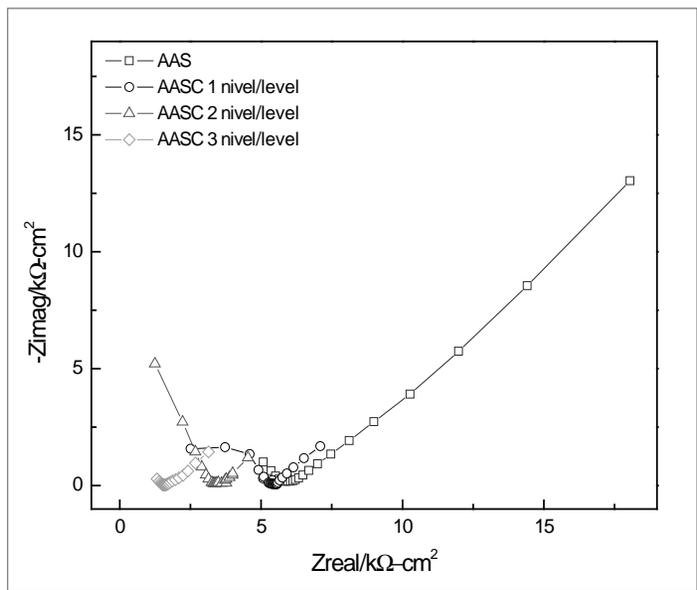


Figura 4. Diagrama de Nyquist correspondiente a los concretos AASC expuestos a carbonatación acelerada
 Figure 4. Nyquist diagram corresponding to AASC concretes exposed to accelerated carbonation

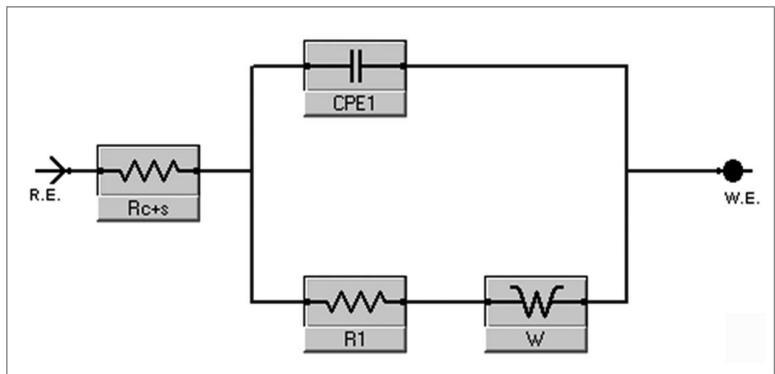


Figura 5. Circuito equivalente del AASC en el nivel 0 de carbonatación
 Figure 5. Equivalent circuit of AASC at carbonation level 0

Tabla 1. Parámetros del concreto AASC en el nivel 0 de carbonatación Rc+s: Resistencia del concreto. R1 y CPE1: Resistencia y capacitancia de la zona interfacial pasta agregados; W (elemento de Warburg): es un elemento electroquímico específico de la difusión. (A. Lasia., 2003;A.A. Sagües; 1987)

Table 1. shows AASC concrete parameters at carbonation 0 level. Rc+s: Concrete resistivity R1 and CPE1: Resistivity and capacitance of aggregate paste interfacial zone. W (Warburg element): specific electrochemical diffusion element (A. Lasia., 2003; A.A. Sagües; 1987)

Parámetros/Parameters	AASC
Rc+s ($\Omega\text{-cm}^2$)	517
CPE 1 ($S*s^a$)	23,1e-9
R1 ($k\Omega\text{-cm}^2$)	10,801
W ($S*s^{(1/2)}$)	211e-3

For AAS concrete under carbonated state, it was found that circuit becomes far more complex due to reactions taking place when material initiates carbonation stage. Figure 5 shows behaviors of concretes under accelerated carbonation from 350 hours up to 1050 hours, period when material reached 100% carbonation. The circuit shown in Figure 7 indicates a first resistivity (R_{c+s}) associated to concrete pores solution, which is found at high frequencies 100 kHz. Then CPE and resistivity are found associated to the first elements in concrete external zone. Such elements can be originated by generated reactions or by surface absorption of some species introducing CO_2 , and then from intermediate frequencies it is possible to find elements such as CPE and resistivity, such elements are associated to paste/aggregates interfacial transition zone in concrete. In low frequency domain the load transference process is normally found, in combination with mass transference process, which correspond to the last R and CPE, such elements are placed in the interfacial transference zone corresponding to concrete and steel. Results obtained are indicated in Table 2.

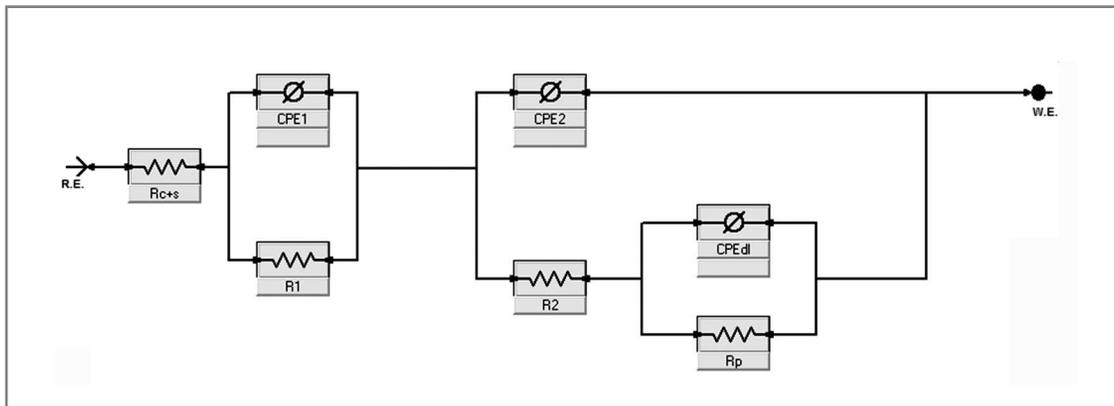


Figura 6. Circuito equivalente para los concretos AASC expuestos después de las 0 horas R_{c+s} : Resistencia del concreto. R_1 y CPE_1 : resistencia y capacitancia de la capa formada por las reacciones; R_2 y CPE_2 : Resistencia y capacitancia de la zona interfacial pasta agregados; R_p y CPE_{dl} : resistencia de transferencia de carga y capacitancia de la doble capa. (D. John et al., 1981; F. Wenger et al., 1987)

Figure 6. XEquivalent circuits for AASC concretes exposed after 0 hours R_{c+s} : concrete resistivity. R_1 and CPE_1 : resistivity and capacitance of layer formed by reactions. R_2 and CPE_2 : resistivity and capacitance of paste/aggregate interfacial zone. R_p and CPE_{dl} : load transfer resistivity and double layer capacitance (D. John et al., 1981; F. Wenger et al., 1987)

Tabla 2. Parámetros del concreto AASC después del nivel 0 de carbonatación
 Table 2. AASC concrete parameters after carbonation level 0

Parámetros/ <i>Parameters</i>	AASC1	AASC2	AASC3
Rc+s ($\Omega \text{ cm}^2$)	133	123	129
CPE1 ($S*s^a$)	0,1431	0,2532	0,396
R1 ($\Omega\text{-cm}^2$)	249	187	141
CPE2 ($S*s^a$)	51,38e-12	7,8e-4	2,47e-
R2 ($\Omega\text{-cm}^2$)	5410	3340	1550
CPEd1 ($S*s^a$)	71,8e-3	56,15e-3	39,96e-3
Rp ($k\Omega\text{-cm}^2$)	125,01	63	9

Table 2 shows that concrete resistivity (Rc+s) at different carbonation levels is quite similar, thus indicating that concrete pores resistivity (denomination for this parameter) has a constant trend. If compared to parameter reported in Table 1 for AAS concrete at 28 curing days and 0 hours exposure, it is noticeable that the latter shows a value four times higher, which indicates that matrix quality was altered by carbonation effect and, therefore, carbonated concrete easily leads to a corrosion process on structural steel. Resistivity R1 value (Table 2), related to reactions developed on the external layer, decreases as long as carbonated concrete thickness is increased. The same behaviour is observed for R2 and Pr resistivities, where it is observed that at longer carbonation time, parameter values are lower. CPE1 and CPE2 capacitance values increase as long as carbonation time goes by; the latter can be attributed to the layer which started to develop on the aggregates interface. Contrarily, CPE1 decreased because steel passivation layer becomes vulnerable as long as concrete carbonation reactions develop.

3.2.2 Natural environmental exposure

In the case of concrete exposed to natural environment, graphs presented in Figure 7 were obtained. Circuits included in Figure 5 are associated for level 0 and, Figure 8 for the rest of levels. Comments related to level 0 were included in above numeral.

Figure 7 shows that AASC concrete trend is contrary to AASA's, so natural exposure allows electrochemical parameters to achieve a higher value thus increasing polarization resistivity, which would deliver a lower value for corrosion speed. When concrete is left under natural environmental conditions, an electric resistivity fluctuation value is observed in comparison to value registered at 28 curing days. Such effect may be explained because material continues its normal hydration process achieving higher compaction and, therefore, carbon dioxide attack - at low level (0.03%) - over concrete surface is remarkably reduced. Contrarily, in long exposure periods the effect of electric resistivity reduction is minimum compared to specimens exposed to accelerated carbonation. The rest of parameters R1, CPE1, CPE2 and R2 are generally increased if compared to AAS. Specifically, polarization resistivity (Pr) - at 1050 hours of exposure under natural environment - (AASA level 3) shows a significant 5 times increase over level 0, meaning there is higher stability of passivation layer on steel surface.

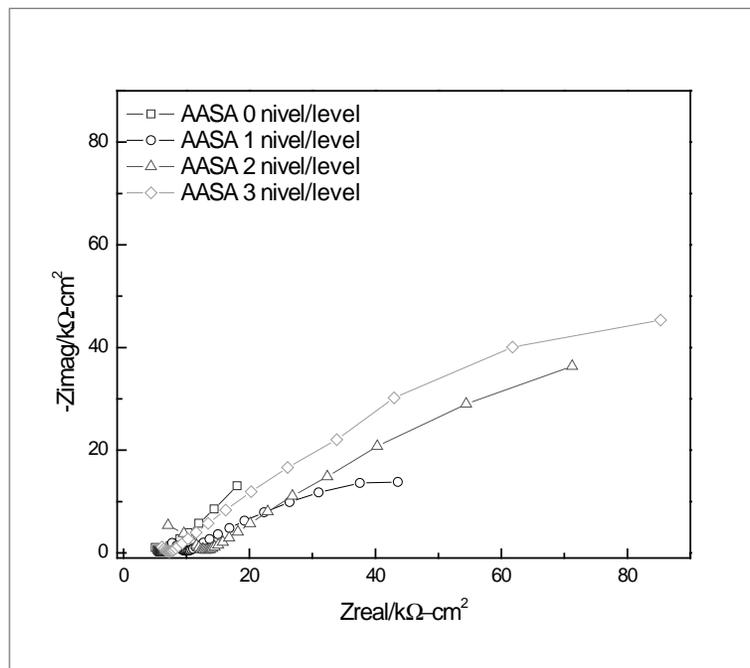


Figura 7. Diagrama de Nyquist correspondiente al concreto AASA expuestos a ambiente natural

Figure 7. Nyquist diagram corresponding to AASA exposed to natural environment

Figure 8 shows the most common circuit for the study of systems involving concretes. Such model is included in several researches as B. Assouli (Assouli et al., 2005), among others. R_{c+s} resistivity corresponds to high frequency domain (between 100 KHz and 1KHz) and it is related to concrete electrical resistivity, also including electrolyte resistivity (electrolyte resistivity is significant compared to concrete resistivity). R_{c+s} may also include contribution effects on surface, i.e interface between electrolyte and concrete. R_1 resistivity corresponds to intermediate frequency domain (from 1kHz to 50 Hz) and it is employed to represent resistivity on transition zone. $CPE1$ corresponds to the representation of non-ideal capacitance in transition zone for cement/aggregate interface, closest to pores. Low frequency domain (50 Hz to 1mHz) is employed to assess load transfer process together with mass transportation process and normally corresponds to R_p resistivity. $CPE2$ is employed to determine non-ideal capacitance of steel surface. Values obtained for such parameters are shown in Table 3.

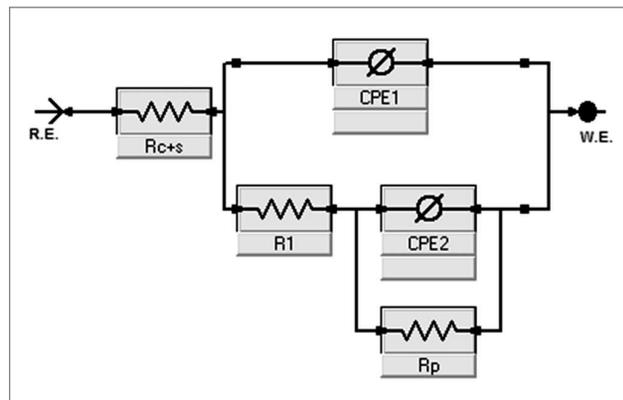


Figura 8. Circuito equivalente correspondiente a los concretos AAS expuestos a ambiente natural evaluados después de las 0 horas
 Figure 8. Equivalent circuit corresponding to AAS concretes exposed to natural environment and evaluated after 0 hours

Tabla 3. Parámetros del concreto AASA después del nivel 0 de carbonatación
 Table 3. AASA concrete parameters after carbonation level 0

Parámetros/ <i>Parameters</i>	AASA1	AASA2	AASA3
R_{c+s} (Ω)	751,8	708	602,7
R_1 ($K\Omega$)	10,005	10,301	10,342
$CPE1$ ($S*s^a$)	0,071e-6	0,0935e-6	0,0405e-6
R_p ($K\Omega$)	40,610	70,133	80,513
$CPE2$ ($S*s^a$)	0,14	0,18	0,918

When concrete is exposed to natural environment, an increase of concrete electric resistivity is observed in relation to 517Ω value registered at 28 curing days (Table 1). Such effect may be associated to the fact that material continues its normal hydration process achieving higher compactation and, therefore, carbon dioxide attack - at low level (0.03%) - over concrete surface is remarkably reduced. Even for long exposure periods, reduction effect on electric resistivity is not significant unlike observations from specimens exposed to accelerated carbonation (Table 2). The rest of parameters - R1, CPE1, CPE2 and Pr - generally increase although at different degrees. Pr polarization resistivity at 1050 hours of exposure period under natural environment (AASA3) shows a significant increase, about 8 times higher than level 0, this means higher stability of passivation layer over steel surface.

4. Conclusions

- Mechanical resistivity of AAS concrete decreases when exposed to an accelerated carbonation process, as it reveals a decreased value for compressive strength compared to value obtained after 28 curing days.
- Carbonation effect on AAS concrete is observed from the very beginning, provided that electrochemical parameters considerably decrease, specially the value for polarization resistivity.
- AAS concretes exposed under natural environmental conditions show an increase of all electrochemical parameters, due to the progress of hydration process itself.
- Electrochemical impedance spectroscopy is an appropriate tool for obtaining detailed information about concrete properties, especially about this material interface. EIS is a convenient technique provided that it can be applied in low conductivity mediums. Simultaneously, it may deliver the following parameters: concrete electrical resistivity, polarization resistivity, double layer capacitance, among others. Changes developed by each interface can be quantified by means of electric circuit equivalence.

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