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Corrosion Evaluation of the Rebar Embedded in Self Consolidating Concrete under Marine Environment

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In this investigation was evaluated the corrosion of ASTM A 706 structural steel embedded in self consolidating concrete (SCC). Two steel bars were inserted in each specimen; they act as working electrode and a graphite electrode at the center of the specimen acts as auxiliary electrode. The environments in which were subjected each concrete were distilled water and water with 3.5 % contents of sodium chloride (NaCl) in weight simulating an aggressive environment. The behavior of the steel was monitored electrochemically by the techniques of linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS). After a six-month exposure under normal and aggressive conditions, the specimens were analyzed using the X-ray diffraction (XRD) technique with the purpose to study in detail the concrete-steel interphase establishing the corrosion products formed during the study. It can be concluded of the electrochemical study that the specimens subjected to NaCl generate a performance status front the specimens subjected to distilled water which have a displacement towards passive corrosion zones.

Keywords: self consolidating concrete (SCC), corrosion, chloride ion, passivation.

1. INTRODUCTION

The main wear process of reinforced concrete in marine environments is the corrosion of the rebar by the action of the chlorides from seawater, being one the wears that induces higher cost in the maintenance and operation of different constructions which are projecting with reinforced concrete [1-3]. The concrete provides to the embedded reinforcement inside of any structural element a protection owing to the coating that it brings; which has to be according with the exposition type that it has and whose function is avoiding the aggressive agents penetration, on the other hand the presenting oxygen in the concrete reacts with the steel forming a thin layer or film of oxide over the reinforcement, this process is known as passivation, thus the reinforcement protects itself of any corrosion type [4-6]. These conditions are efficient as long as the concrete keeps its alkalinity and high resistivity values, otherwise is possible that the reinforced steel presents corrosion. In order to this phenomenon develops is required a current flow generated inside the concrete by humidities differential and presence of oxygen or electrolytes concentration. The previous problem has resulted to be a main topic for the researchers focused in construction materials from the standpoint of durability of such structures, in the search of increase in the useful life of the civil structures, particularly those located in favorable environments to deterioration such as the marines [7-8].

Currently, the studies are focused in find a system that decreased the corrosion velocity, among these studies are found the handling of pozzolanic materials inside the concrete, but are few researches which have studied the self consolidating concrete (SCC) as material that due to its mechanical composition brings a decrease of the empty spaces inside the composite material [7], [9-11].

The time and quality of the cured affect significantly the inclusion of chloride ion quantity, inasmuch as a good cured contributes to decrease of the porosity and the pores connectivity particularly close to the concrete surface. Gowripalan et. Al [12], found that the initial cured is critic in the coating permeability reduction of the concrete, therefore, decrease in the corrosion by the immersion of the chloride ion [9].

In the present research shows the behavior of the self consolidating concrete (SCC) against the corrosive phenomenon of the reinforcement armor, using nondestructive electrochemical techniques as linear polarization resistance, Rp (LPR), for the characterization of the corrosion velocity and as complementary tests were performed chloride permeability tests.

2. EXPERIMENTAL DETAILS

The self consolidating concretes (SCC) were prepared with a water cement/relation of 194 liters/m^3, the relation water/fines in volume was 0.90, the aggregates used correspond to a gravel with a maximum size of 19 mm, specific gravity of 2940 kg/m^3, unitary mass compacted of 1860 kg/m^3, loose unitary mass of 1700 kg/m^3, and absorption of 1.3%. A sand with specific surface of 2470 kg/m^3, unitary mass compacted of 1670 kg/m^3, loose unitary mass of 1580 kg /m^3, and absorption of 2.9%.

As working electrode was used colombian commercial structural steel (ASTM A706) commonly used in earthquake-resistant construction, with a diameter of 1/8” and without previous treatment. For the development of the electrochemical tests was used an external reference electrode of copper sulfate copper (Cu/$CuSO_4$) of analytic type. A graphite electrode immersed in the specimens (during the fabrication) acts as auxiliary electrode. The samples used in the study were fabricated using the specified materials above and according to the design shown in figure 1, all the specimens have the same size and geometric arrangement.

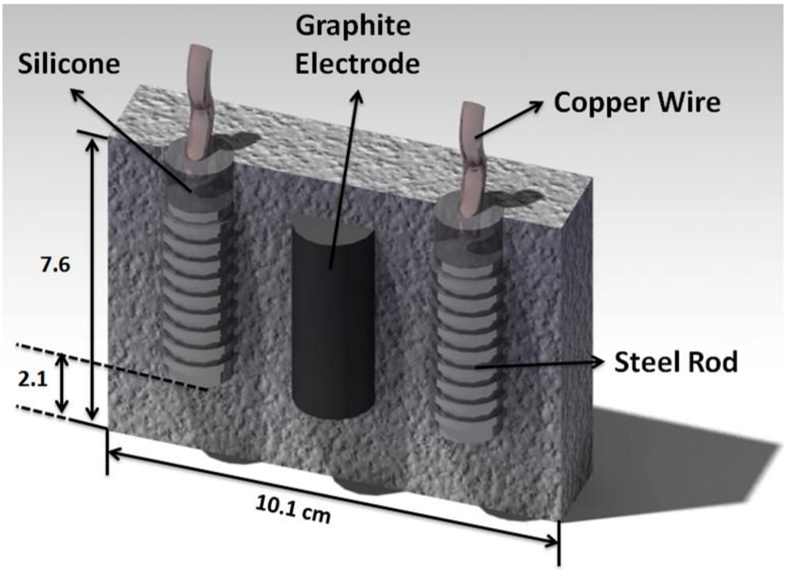

Figure 1. Probes geometry.

Once the curing of the materials is complete, the specimens were introduced in two environments. For simulated standard conditions the specimens were immersed in distilled water the whole time. In contrast with the purpose of reproduce aggressive conditions, the concretes were placed in immersion in a mixture with 3.5% of analytic sodium chloride (Panreac PA131655.1211 NaCl-99.0%) during the same time.

Inasmuch as the free chloride ions in the solution were consumed after an exposition time, starting of a preliminary study was established that the electrochemical condition of the system returns to nonaggressive values after twenty days; [13] for this reason the electrochemical tests had this time interval to each other.

The electrochemical measurements were done during twelve months with intervals of twenty days. The AC/DC tests were performed with the Gamry PCI-4 equipment. Tests of linear polarization resistance (LPR) were performed by applying a small external potential (±20mV), around the open circuit potential. In the electrochemical impedance spectroscopy (EIS) studies was used a sinusoidal signal of 10mV effecting a scan of different frequencies from 10 kHz to 1 mHz. [14]

Corrosion products generated on the surface were identified of the steel by X ray diffraction (DRX). The experimental arrangement in X ray diffraction correspond to a PW3050/60 goniometer (θ/θ), handled under a XPERT-PRO system using a monochromatic radiation of Cu Kα 1,54 Å, operated at 40 kV y 40 mA under temperature conditions of 25°C. The scan over the surface was performed from $2\theta = 20.01°$ to $2\theta = 99.99°$ with a step $2\theta = 0{,}02°$ at a scanning time of 1 second. The crystalline phases of the steel surface was done with a XPERT-PRO X ray difractometer, using the diffraction database of the equipment, furthermore the MAUD program which is a analysis program based on the Rietveld method, this method consists in adjusting a theoretical diagram in order that fully match with the observed. Those theoretical diagrams were obtained with base to crystalline structures and in a series of crystalline parameters. These phases found were compared with those reported by other researchers [14].

Cylindrical specimens (76.2 mm diameter and 152.4 mm length) were used to test the materials for compressive strength according to ASTM C 42-04 Standard [15], absorption and voids in hardened concrete according to ASTM C 642-06 Standard [16], and chloride permeation according to ASTM C 1202-07 Standard [17].

3. RESULTS AND DISCUSSION

3.1 Compressive Strength Test

Figure 2 shows compressive strength versus age of curing the results for specimens chlorides without (after 28 days of curing), for specimens after exposure to accelerated an chloride ion and without exposure (1 year after curing). The compressive strength results are the average values for three specimens. It can be observed that the highest compressive strength (43.25 MPa) is shown by the specimen after 28 days age of curing in the absence of chloride ion. The lowest compressive strength (36.59 MPa) is shown by specimen exposed to effect of chloride contamination. In contrast, on specimen without exposure to chlorides the highest compressive strength (47.32 MPa), see Fig. 2.

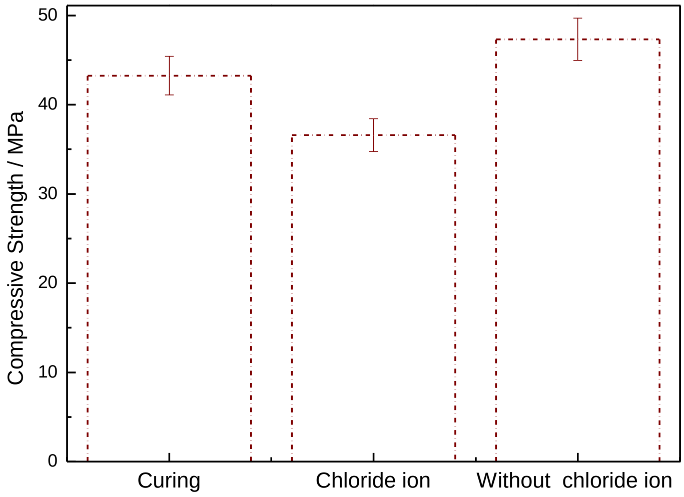

Figure 2. Compressive strength versus age of curing for the consolidating concrete with and without immersion to chloride.

3.2 Permeable Voids and Water Absorption Test

$$Permeable \ \ Voids = \left(\frac{A-B}{V} \right) \times 100 \quad (1)$$

The oven dried cubes after attaining constant weight, then they were immersed in water and the weight gain was measured at regular intervals until a constant weight was reached. The water absorption at 30 min, initial surface absorption, and final absorption, at a point when the difference between two consecutive weights at 12 h interval was almost negligible, was determined. The final absorption in all cases was determined at 96 h.

Figure 3 shows permeable voids, calculated using Eq. (1), and water absorption results, for the self-consolidating concrete. The lowest permeable voids percentage is observed on the concrete see Figure 3. This behaviour may be attributed to segregation resistance and containing aggregates which generates the homogeneity of the concrete. These results agree well with results in the literature [18].

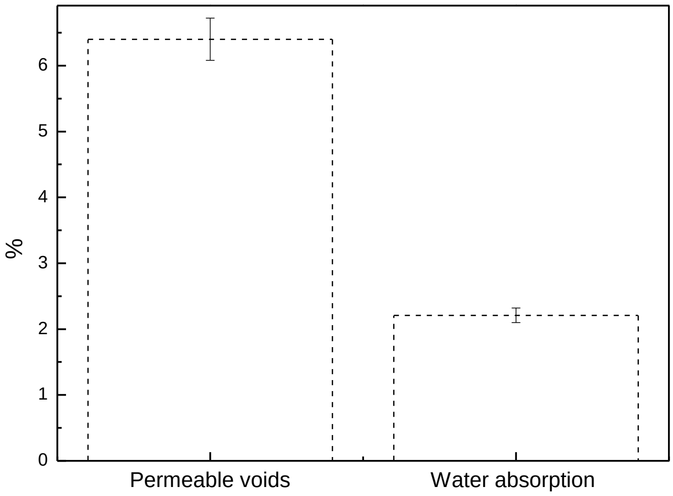

Figure 3. Permeable voids and water absorption for the Self-consolidating concrete.

3.3 Accelerated Chloride Ion Permeability Test

Accelerated chloride ion permeability test was performed according to ASTM C 1202-07 Standard [19]. This accelerated chloride ion permeability method has been severely criticised because of its severe testing conditions which may cause both physical and chemical changes [19]. The specimen used was 100 mm diameter × 50 mm length. A potential difference of 60 V DC was maintained across the specimen, which generates a non-steady state migration flux of chloride ions through the concrete. Concrete slices of 50 mm thick were cut from the centre of the specimen in order to avoid heterogeneity and then just before the non-steady state migration test, they were water-saturated under vacuum. One of the surfaces was in contact with a 3% by weight of sodium chloride (NaCl) solution (anolyte) and the other with a 0.3 N of sodium hydroxide (NaOH) solution (catholyte). The total charge passing through in 6 h was measured, indicating the degree of resistance of the specimen to chloride ion permeation. Resistivity (ρ) (Ω cm) can also be determined from the initial current reading (I) using Ohm’s law:

$$R = \frac{V}{I} \tag{2}$$

where *R* is resistance, and *V* is voltage. The ρ is determined:

$$\rho = \frac{RA}{l} \tag{3}$$

where A is area of the disc and l is thickness of the disc. Table 1 includes initial current, resistivity, and total charge passing for the concretes investigated.

Figure 5 shows the total charge passing in 6 h as a measure of the chloride permeability. The chloride ion penetrability limits suggested by ASTM C 1202-07 Standard were compared with the results. It can be seen that all self consolidating specimens showed less or equal than 1000 Coulombs total charge passing and these were assessed as very low penetrability. The self consolidating concrete with and without immersion to chloride, showed values in the range "very low" to "moderate" according to the assessing criteria, dotted lines in figure 5 [17]. Results of figure 5 indicate that self consolidating concrete performed better with respect to chloride penetrability. The resistivities calculated by considering the initial current through Eq. (3) also followed a similar trend as the total charge passing (see Table 1).

Table 1. Tests of absorption, porosity and density of the self-compacting concrete.

Concrete	Absorption after immersion (%)	Absorption after immersion and boiling (%)	Dry Density (g/cm^3)	Density after immersion and boiling (g/cm^3)	Apparent density (g/cm^3)	Permeable pore volume (%)
Curing	2.12	2.67	2.54	2.63	2.71	7.4
Chloride Ion	2.16	3.21	2.65	2.67	2.79	8.2
Without chloride ion	4.42	4.81	2.45	2.64	2.71	12.6

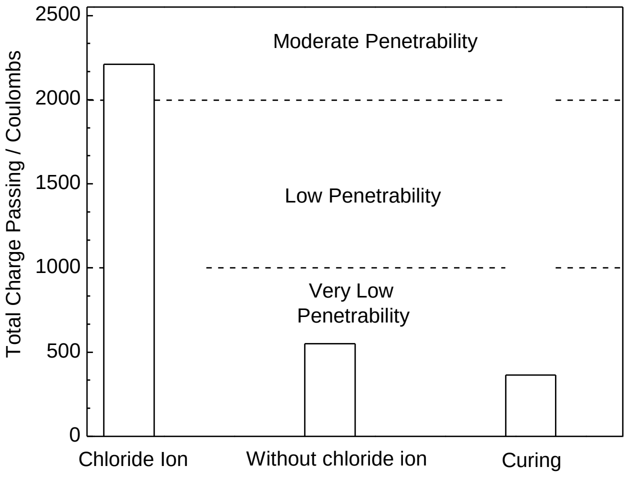

Figure 4. Values of chloride permeability of concrete for the different concretes.

The test performed following ASTM C 1202-07 Standard which is mainly a measurement of electrical conductivity that depends on pore structure and chemistry of pore solution. For the experimental conditions tested (specimen size and applied DC voltage), the initial current can be regarded as a representative of electrical conductivity of the specimen. Table 1 indicates that specimens exhibit higher electrical conductivity than self consolidating specimens.

3.4 Polarization Resistance

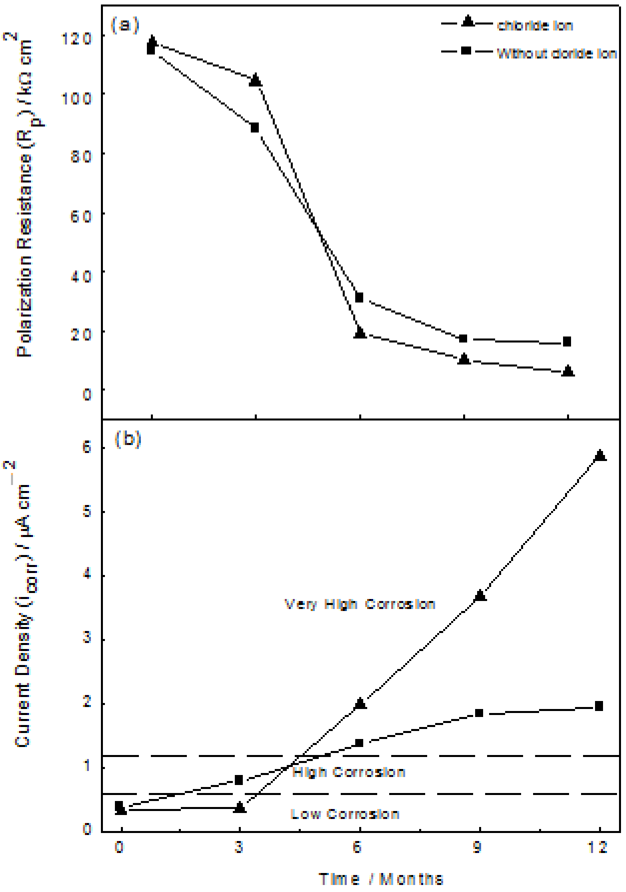

Figure 5. Polarization resistance and current density of the self consolidating concrete with and without chloride ion.

In the figure 5 shows the polarization resistance of the sample evaluated at 0 hours of exposition (28 days of curing) environment, the evaluted samples presents that value (115 kΩ-cm^2) since on this exposition time have been generated the protection layer on the steel surface. Subsequently a series of this concrete is exposed to a solution with chloride ion and other just with water. The subjected specimens to the mixture without chloride ion exhibit a decreasing behavior on the polarization resistance value, which indicates that the protection layer being compromised, this trend is kept until the fourth level (9 months), Inasmuch as at the 12 months, this behavior changes generating a greater estability to the protector layer cause of the estabilization of the polarization resistance. The self consolidating concrete subjected to a chloride ion mix shows the same behaviour that the exposed without chloride since the polarization resistance value decreases abruptly, the Rp value is always minor than the studied without chloride ion, which indicates that the chlorine ion generates a greater degradation value of the embedded steel in the self consolidating concrete than the embedded steel in the same concrete, but without chlorine content, it is observed for all studied exposition times. Using the criterion of the corrosion current proposed by C. Andrade (2002) [20] for the prediction of steel state. It can state that those materials with an without choride ion subjection, after six months of evaluation suffer of high corrosion velocity since its current exceeds 1 $\mu A/cm^2$.

3.5 Electrochemical Impedance Spectroscopy

In the figure 6 is observed the Nyquist diagrams corresponding to the self consolidating concrete with chloride ion content, this yields a decrease of all electrochemical parameters found, in special the solution resistance and polarization resistance, in the first evaluated level is found a high decrease due to the entry of the chlorine ion in the concrete, the same behavior is observed for the others studied levels in which a reduction is found by the displacement to the left of each of the Nyquist diagrams. To model the found elements in this analysed system, we used the showed circuit in the figure 7, which is used to explain electrochemically the chorine ions effect over the rupture of steel passivity, this model is the best that adjusts in our study since in the first resistance is found the opposition of the ions in the mixture; when chloride ions enter into the concrete, this value is low for the first levels since the quantity of ions on the first levels is minimun, therefore chloride ions enter easyly, then in the subsequent levels these concretes are saturated of aggressive misture hence this value increase, then it is shown a resistance (R_1) which is generated in the interphase of concrete/aggregates; the resistance value changes depending of the evaluated level (table 2), therefore in the first levels is generated a higher resistance of the ions when passing through the aggregates, this resistance begins to decrease inasmuch as the concrete resistivity begins to decay when has been entered chlorine ions in the system, in the same interphase is found parallel to the R_1 the constant phase element CPE_1 which acts as a capacitor with the condition of the superficial imperfections found in this interphase, this CPE value for each case is high, hence the ions generates other path which is represented by the found resistance among the concrete and the passivating layer of the steel [21]. The polarization resistance value (R2) is minor each time owing to the opposition in the first levels is greater, for this reason the passivation layer which is found in the system; this layer begin to be compromised after certain quantity of chlorine ions have entered through the interphase, i.e. as increase the percentage of chlorine in this interphase, accordingly the polarization resistance value is minor each time, which indicates an increase in the corrosion velocity, the constant phase element correspond to this interphase which is parallel to the polarization resistance that shows a decrease of this parameter. The phenomenon is generated in this case since each level that this element offers a greater pace of the ions generating the wear that occurs on the steel surface.

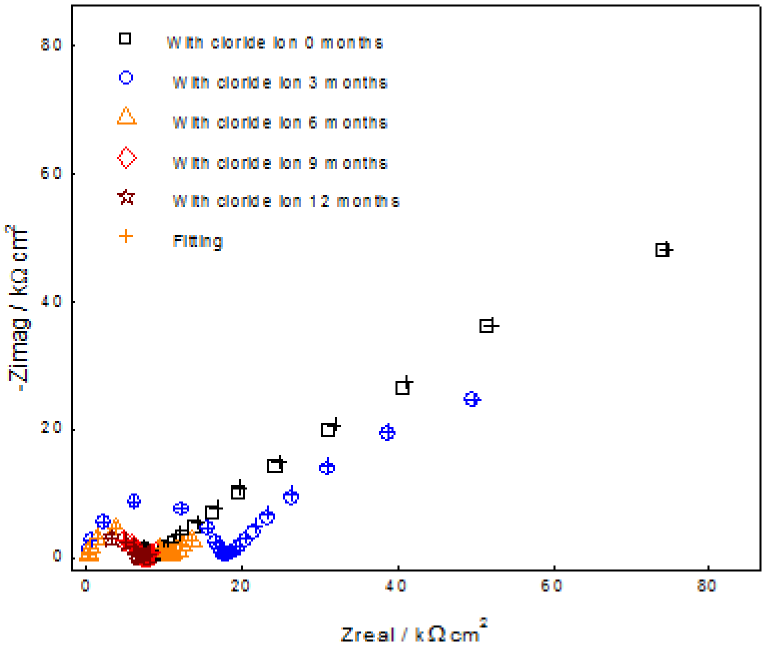

Figure 6. Nyquist diagram corresponding to self consolidating concrete with chloride ion exposition.

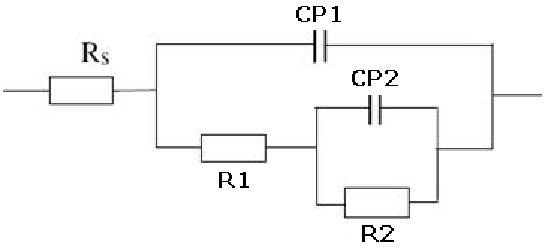

Figure 7. Equivalent circuit fitting circuit for the impedance data of self consolidating concrete.

The self consolidating concrete subjected to a fluid without chlorine content, shows a similar behavior to found for this same concrete, but in a fluid with chloride ion (figure 8), since both contain the same elements that shape the electrochemical behavior, the difference lies in which the behavior is different in this study case, therefore the found elements show a greater value in each one of analyzed levels, furthermore the behavior at the twelve months is different since the studied parameters do not continue to decline but increase in comparison with the six months of evaluation, cause the passivation layer is regenerating which forms a new protection against corrosives phenomena, also this is due to the mix that in the beginning destabilized the protective layer to cause the found reactions, it is not noxious because did not contain chloride ion, which is a corrosive agent in the concrete. As it is observed in the table 2, the solution resistance which is the found resistance between the concrete and the mixture is low in the first 3 months, hence in the beginning the mix enters with low limitation, then in the next months the concrete is saturated of combination, accordingly the quantity of ions that will pass for this established parameter are less; The R1 decreases its value according as the analyzed levels increase, this is owing to in the beginning the solution/aggregates interphase was oppose to the ions pass, then this system allows the pass of ions more easily due to the concrete resistivity becomes lower by the entry of the combination that reacts with aggregates.

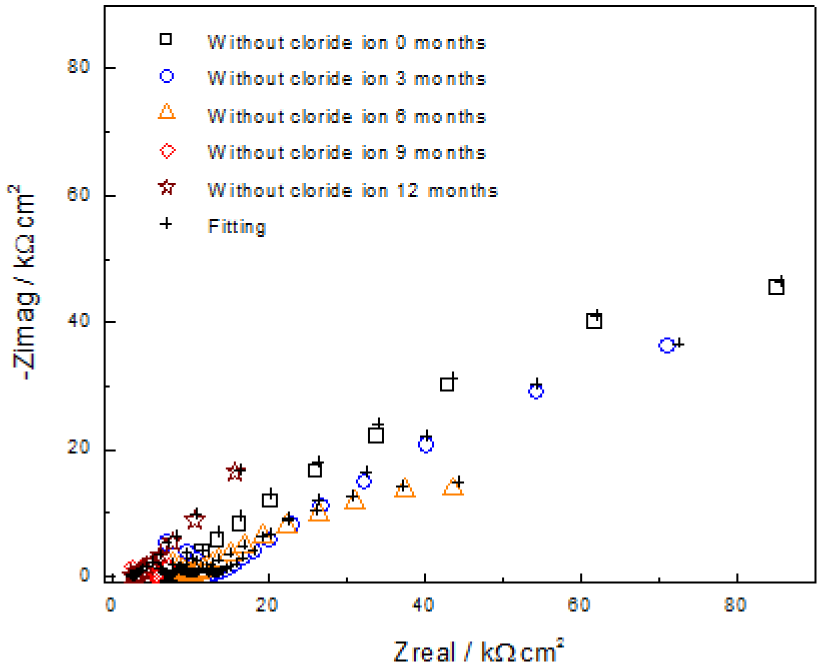

Figure 8. Nyquist diagram corresponding to self consolidating concrete without chloride ion exposition.

Table 2, Parameters used in the fitting of impedance data for steel rebars embedded in self consolidating concrete with and without chloride ion.

Time Months	R_Ω Ω cm^2	Y_{P1} F cm^{-2} s$^{-(1-\alpha_1)}$	α_1	R_1 kΩ cm^2	Y_{P2} F cm^{-2} s$^{-(1-\alpha_2)}$	α_2	R_2 kΩ cm^2
SCC without chloride ion							
0	73.3	2.4×10^{-8}	0.72	49.435	4.54×10^{-4}	0.69	136.25
3	83.5	$2,56\times10^{-8}$	0.84	43.67	63×10^{-4}	0.76	122.61
6	76.4	4.56×10^{-8}	0.82	32.45	75×10^{-4}	0.78	111.3
9	40.6	7.54×10^{-8}	0.83	11.72	84×10^{-4}	0.77	67.21
12	27.3	2.71×10^{-8}	0.92	9.46	165×10^{-4}	0.82	26.75
SCC with chloride ion							
0	64.3	2.9×10^{-8}	0.78	51.9	7.34×10^{-4}	0.73	142.34
3	66.7	3.40×10^{-9}	0.84	21.13	9.27×10^{-4}	0.83	95.42
6	62.4	3.54×10^{-9}	0.85	10.80	12.7×10^{-4}	0.81	51.4
9	64.1	4.21×10^{-9}	0.89	3.34	16.3×10^{-3}	0.79	25.7
12	69.1	5.34×10^{-9}	0.85	2.52	18.5×10^{-3}	0.86	12.4

The polarization resistance has a gradual decrease as the analyzed level advance; this is due to the mix entry as far as the concrete/steel interphase which generates a degradation of the protective layer that in the beginning is high, later becomes to be minor for this reason the layer itself starts to reconstructed inasmuch as the combination that has entered is not aggressive, therefore it generates a conformation of a protective layer which is corroborated by the generated measurement of the twelve months in where the parameters corresponding to concrete/steel interphase change the direction.

3.6 X-ray diffraction

The figure 9 shows the DRX spectrums corresponding to the self consolidating concrete with and without exposition to chlorine ion, it can be found the following present phases: C: calcite, G: goethite, AN: Andradite, H: halite, MG: magnetite, W: wüstite, L: lepidocrocite, HM: hematite and Q: quartz.

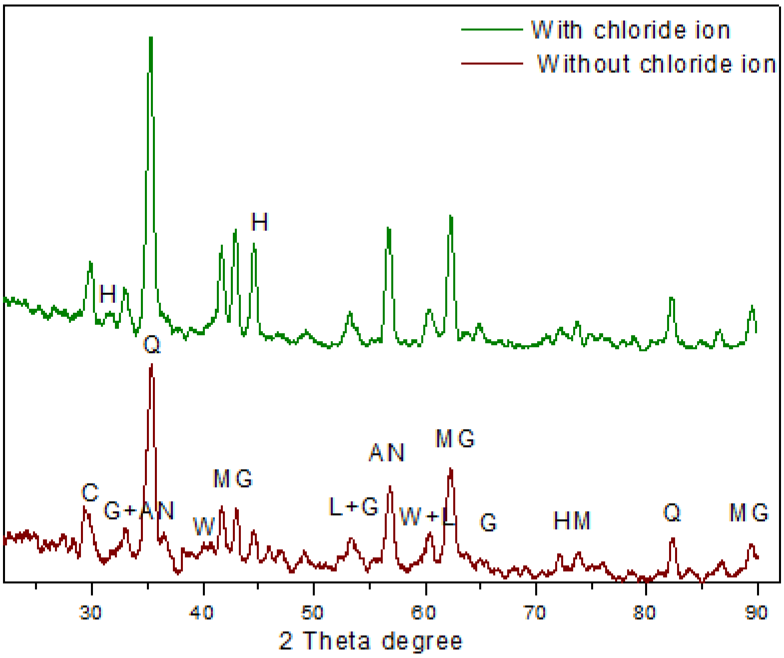

Figure 9. XRD corresponding to the SCC with and without exposure to chloride ion.

The two analyzed systems present similar phases, the different lies in the found intensity in each one of the peak, due to the immersed systems in chloride ion the intensities are higher. The peak corresponding to the Q phase presents a high intensity; it is attributed to the concrete matrix (cementitious material and aggregates). The found oxides over the steel surface are MG and W, it is observed that are the phases which are presented with the higher intensity respect to the other excluding the quartz; the found hydroxides belong to G, L and HM. Both the oxides and hydroxides registered in those spectrums are occurring in most corrosion processes which present the embedded steel in self consolidating concrete. Nevertheless, an additional phase was found in this study which is the halite that is manifested by the chlorine content over the surface due to the chlorine ion in those specimens have already reached the interface. The spectrum corresponding to self consolidate concrete in absentia of chloride ion, including in the same figure 8 as well, presents in general the same phases with lower intensity excluding the corresponding to the halite phase.

4. CONCLUSIONS

Comparing the electrochemical behaviors of the self consolidating concrete with and without chloride ion, is observed that the best behaviors are the espoused specimens to a solution without chlorides, since exhibit a restoration behavior of the protective layer inasmuch as its electrochemical parameters increase in each one of the evaluated levels, in contrast to the self consolidating concretes subjected to chloride ion, which generate a steel degradation and a decrease of each one of the found parameters, although in a low magnitude.

To estimate the embedded steel degradation in the self consolidating concretes, it was determinate the oxides and hydroxides of iron presence in all of the analyzed samples, deriving corrosion products such as (magnetite (Fe_3O_4), Wüstite ($Fe^{2+}O$) and goethite ($Fe^{3+}O(OH)$). The exposed concretes to chlorine ion show a increase in the corrosion products in comparison with these same materials, but subjected to a mix without chlorides due to chlorine effect over the concrete which removes the passivation layer and generates general corrosion.

References

1. D.M. Bastidas, A. Fernández-Jiménez, A. Palomo, J.A. González, *Corrosion Science,* 50 (2008) 1058.
2. M. Moreno, W. Morris, M.G Alvarez, G.S Duff, *Corrosion Science*, 46 (2004) 2681.
3. W. Aperador, R. Mejía de Gutiérrez, D. M Bastidas. *Corrosion Science*, 51 (2009) 2027.
4. T Vidal, A Castel, R François, *Cement and Concrete Research*, 34 (2004) 165.
5. L. Abosrra, A.F. Ashour, M. Youseffi, *Construction and Building Materials*, 25 (2011) 3915.
6. M. P. Enright, D. M. Frangopol, *Engineering Structures,* 20 (1998) 960.
7. Ha-Won Song, Velu Saraswathy, *Int. J. Electrochem. Sci,* 2 (2007) 1.
8. D. Nieves-Mendoza, C. Gaona-Tiburcio, H. L. Hervert-Zamora, R. Tobias, P. Castro-Borges, R. Colas, P. Zambrano Robledo, A. Martínez-Villafañe, F. Almeraya-Calderón, *Int. J. Electrochem. Sci*., 7 (2012) 5495.
9. A.A.A. Hassan, K.M.A. Hossain, M. Lachemi, *Engineering Structures*, 32 (2010) 874.
10. H.A.F. Dehwah, *Construction and Building Materials*, 37 (2012) 277,
11. Muhammad Wasim and Raja Rizwan Hussain, *Int. J. Electrochem. Sci*., 8 (2013) 1678.
12. N. Gowripalan, V. Sirivivatnanon, C.C. Lim, *Cement and Concrete Research*, 30 (2000), 725.
13. T. Yonezawa, V.Ashworth, R. P.M Procter, *Corrosion,* 44 (1988) 489.
14. I. Martínez, C. Andrade, *Corrosion Science*, 50 (2008) 2948.
15. ASTM C 42/C 42M-04 Standard, Standard test method for obtaining and testing drilled cores and sawed beams of concrete, West Conshohocken, PA, American Society for Testing and Materials, 2004.
16. ASTM C 642-06 Standard, Standard test method for density, absorption, and voids in hardened concrete, West Conshohocken, PA, American Society for Testing and Materials, 2006.

17. ASTM C 1202-07 Standard, Standard test method for electrical indication of concrete's ability to resist chloride ion penetration, West Conshohocken, PA, American Society for Testing and Materials, 2007.
18. F. A. Sabet, N. A. Libre, M. Shekarchi, *Construction and Building Materials*, 44 (2013) 175.
19. M. Uysal, K, Yilmaz, M. Ipek, *Construction and Building Materials*, 27, (2012), 263.
20. C Andrade, C, Alonso, J. Sarría, Cement and Concrete Composites, 24 (2002) 55.
21. L. Dhouibi, E. Triki E and A. Raharinaivo, The application of electrochemical impedance spectroscopy to determine the long-term effectiveness of corrosion inhibitors for steel in concrete Cement and Concrete Composites, 24 (2002) 35