Int. J. Electrochem. Sci., 10 **(2015)** 4585 - 4595

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Improved Protection against Corrosion of Galvanized Steel Embedded in Alkali-Activated Concrete

W. Aperador[*], *M. Plaza, A. Delgado*

School of Engineering, Universidad Militar Nueva Granada, Bogotá-Colombia
[*]E-mail: william.aperador@unimilitar.edu.co

Received: 24 February 2015 / *Accepted:* 12 April 2015 / *Published:* 28 April 2015

This research evaluates the corrosion resistance of a galvanic steel bar embedded in an alkali-activated concrete. The non- destructive electrochemical techniques for measure of corrosion rates of steel bar embedded in concrete include linear polarization and impedance spectroscopy measurement. The work to be describe on this paper concerns the application of linear polarization to steel bar ASTM-A706 embedded at solution of NaCl de 3,5 wt. %, within alkali-activated concrete. The aim was to relate the response of variation of corrosion in the transition state from passive to active of the steel bar.

Keywords: corrosion, alkali-activated concrete, galvanized steel.

1. INTRODUCTION

Slag specimens on concrete and chemical composition of a pozolanas are used a direct replacement for Portland cement in concrete. Portland cement replacement takes advantage of the energy invested in the slag making process and its corresponding benefits in cost production [1]. It has been generally shown that concretes containing metallic slag as a cement replacement, at normal temperatures, develop low resistance that made from Portland cement at early ages [2].

Chemical activation refers to some chemical substances to accelerate the potential reactivity and to increase the rate of hydration. Some chemical activator is clinker has influence on the resistance of the compression, cement mass and reduction of the porosity compare with the cement Portland [3]. Laboratory research demonstrates that many metallic slag can be activate with some chemical activator as clinker has influence on resistance to the compression [4]. Blast furnace Slags are nonmetallic by products of many metallurgical operation [5]. Ferrous slags are produced through iron and steel manufacturing coke at 1400 - 1600°C. Molten slag is cooled to a solid crystalline form by CA-Al-Mg.

ß dicalsium silicate are stable in blast furnace slag and it is reported as the only constituent of cement product [6].

Blast Furnace Slag is formed by mean of two processes. Granulated slag is rapidly cooled by large quantities of water under pressure (0.6 MPa) to produce a sand-like granule. In this process, 1 ton of slag consumes about 3 m^3 of water [7].

The other process developed on Canada is the pelletized or expanded slag is quickly cooled using water or steam to produce a lightweight product. Water consumptions around $1m^3$ per ton of slag and residual water content in the slag is only about 10% [8]. Blast furnace slag was activated by the use of alkali solution. The reaction product obtained is a product used on concrete. The initial and final time of set of concrete are influenced by concrete/activate substances temperatures. The reactions which occur are mostly exothermic, that is, the reactions generate heat [9].

The steel-reinforced concrete is one of the most important materials employed in public works and building construction projects and a countless number of concrete structures have been constructed worldwide [10]. However, strength of concrete is marginally affected by conditions where problems on reinforcement corrosion due to the ingress of chloride ions of concrete have arisen and some of the concrete structures are affected by hard deterioration actions in very severe environment.

An evaluation of durability in steel slag concretes and the corrosion of reinforcement due to the ingress of chloride ions which are supplied from marine environment (3.5% NaCl), is a typical and one of the most severe deterioration on concrete structures [11]. The results are reported from the evaluation of corrosion rate and electrochemical properties of galvanized and not galvanized steel embedded in concrete specimens contaminated with different concentrations of NaCl (3,5% wt) and exposed to a simulated marine environment.

The monitoring of the linear polarization resistance technique, and the electrochemical impedance spectroscopy (EIS), were used to evaluate the corrosion behavior of the steel bar at different exposure times.

2. MATERIALS AND METHODS

The effect of silicate content (SiO_2/Na_2O) with 5% de Na_2O and SiO_2/Na_2O ratio of 2.4 as activator on physical and mechanical properties of alkali-activated blast furnace slag paste has been investigated. Coarse aggregate type as well size was the same for both type of concrete. Bead size corresponds with the gravel of 19 mm, specific gravity 2.94, body Mass compact unit 1.86 kg/cm^3, loose unit mass1.58 kg/cm^3 and Absorption of 2.9%. The activated slag's mixture curing it was conditioned a controlled environment, with relative humidity of 90% and constant temperature of 20 °C [12].

Low carbon is used as a substrate due low cost and commonly used in structure construction. The chemical compositions of these stainless steels are shown in table 1.

Table 1. Chemical composition of steel ASTM A706, used as substrate.

	Composition (weight %)				
Steel ASTM A706	C	Mn	P	Si	S
	0.20	0.39	0.042	0.19	0.035

Zinc is also widely used today in Electrodeposition process. Electroplating is a process in which zinc is electro deposited onto the steel surface. This method is widely used for applying coatings onto large-sized material. The Chemical composition of zinc is of 99.5%. Zinc alloy chemical composition standards are defined on table 2 [13].

Table 2. Zinc alloy chemical composition

	Pb	Cadmiun	Iron	Tin
Zinc 99.5%	0.45	0.15	0.03	0.005

Trichloroethylene has used as a metal degreasing agent at 25ºC during 30 minutes, then rinsed in distilled water for 2 minutes, then a pickling process on stainless steel with pickling solution of HCl (50 %) and H_2O (50%), an proceed to wash and rinse with distilled water. Subsequently forms a coating surface with fluxing material. Fluxes facilitate the reaction occurs at the surface of the metal and it has been used to activate the metal surface for subsequent reaction with zinc metal (fluxing works forming zinc ammonium chloride at a melting point). Electroplating has been carried out in Combined working standard solution using 80g/l of NH_4Cl and 20 g/l of Cl_2Zn to a temperature 25ºC selectable in 1 minutes.

Step is performed by means of an induction heating system at 80ºC for a period of time of 3 minutes. Finally, hot dip galvanization was used in a molten zinc bath at 465ºC for a period of time of 1 minutes with output of 25.4 cm/s [14].

The ASTM A 706 structural steel as a working electrode was used with an exposed diameter of 1/8” frequently used in making some earthquake resistant structures. Electrochemical test measurement technique was developed using a silver wire coated with silver chloride (Ag/AgCl) reference electrode BAS (MF-2052 RE-5B). A counter electrode of graphite rod was immersed directly in the test solution. The samples resulting from the study- specific sample design (fig 1) [15].

Effect of Chloride ions on the corrosion of galvanized steel used, in reinforced concrete were analyzed using a previous treatment. For standard test method of aggressive condition, after completing the setting of materials, concretes were immersed in a 3.5% sodium chloride (NaCl) solution (Panreac PA131655.1211 NaCl-99.0%) for 1 year period of evaluation.

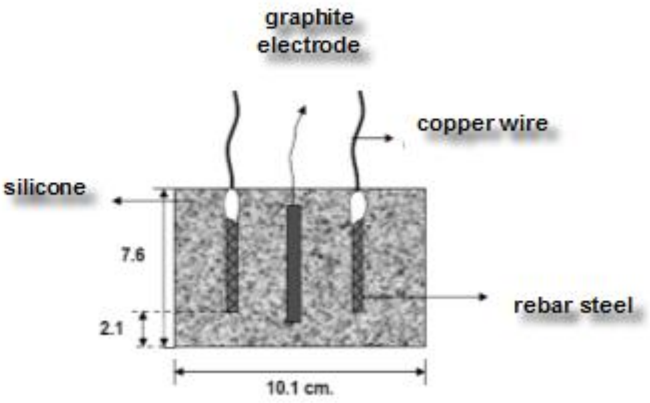

Figure 1. Test system for electrochemical techniques

During the development of the analysis, were subjected to chlorination at different initial free chlorine in the solutions [16]. The amount of free chlorine Solutions concentration was consumed after times of exposition, in preliminary studies has been shown that the electrochemical condition of the system returns to nonaggressive values after 90 days. For this reason the electrochemical tests had this time interval to each other. Electrochemical impedance measurements were performed during for twelve months whiten period of 30 days. Electrochemical study was carried out with a Gamry Model PCI 4 [17]. Linear Polarization Resistance (LPR) tests were performed using an electrode probe by applying a small potential in the range of 20 mV on these electrodes. Electrochemical impedance spectroscopy is a recent tool in corrosion. In the research EIS test, a small (1 to 10 mV) AC signal is applied to the cell at range frequency of 0.1 mHz to 10kHz.

3. RESULTS AND DISCUSSION

3.1 Linear Polarization Resistance. (*LPR*)

Polarization resistance results obtained in this study of the two byproducts were used a Steel embedded in concrete, the passive and active properties and behavior of steel were been well established. in-Situ analysis of corrosion behavior of steel system is used to explain the corrosion behavior, based on the parameters of LPR and Ohm's law. Thus, the corrosion potential remains constant, we can conclude that a low resistance allows easy passage of high current signals [18].

Low Polarization resistance (Rp) values determined from linear polarization tests for coated specimens means the high corrosion and vice versa, related with the loss of metallic particles.

Table 3. Initial Polarization resistance (Rp)

System	Rp (kΩ-cm^2)
Coated	121.2
Un-coated	42.4

Polarization resistance curves for different materials show considerable variations on electrochemical conditions. (table 3), That means cases can be easily explained using its own characteristics of activity and passivity.

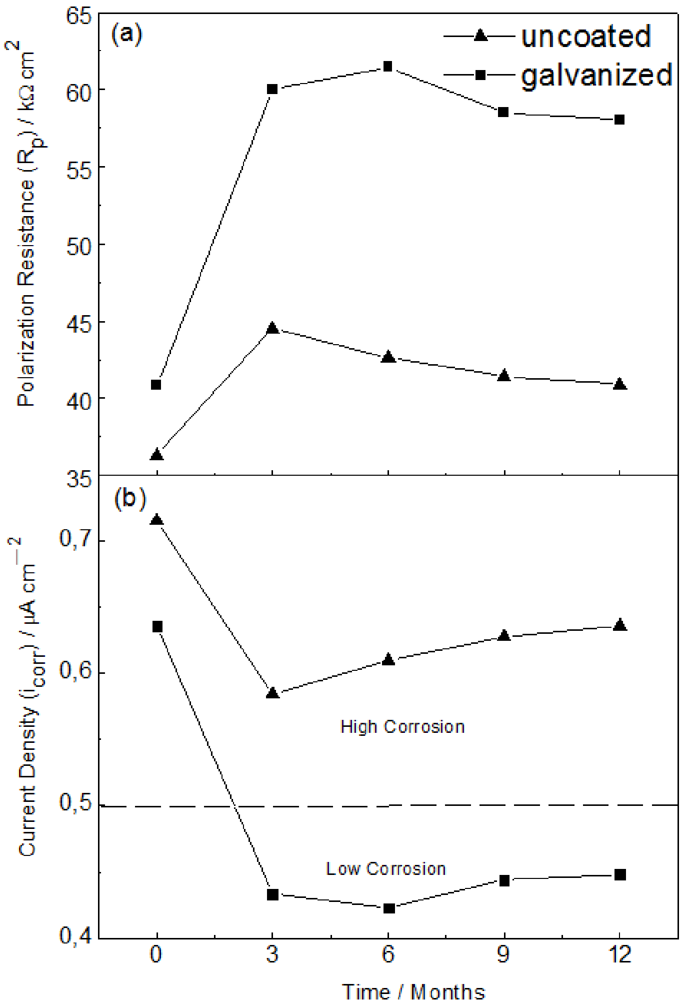

Figure 2. Rp variation for different systems by LPR technique.

The polarization resistance Rp is defined as the slope of the linear part of the Polarization curve close to the corrosion potential Ecorr. Large value of Rp slope corresponding to changes in the rates of the corrosion reactions. Process conditions contribute to corrosion in study cases, since corrosion is time dependent it may take a one years for corrosion problems to become apparent and correct methods to prove the research theory.

New characteristics can be achieved by comparison of electrochemical data results for new coating and surface treatment, Additional the corrosion taking place on steel with the passage of time. Coated and uncoated reinforcing steel embedded in concrete was test under simulated marine (3.5% NaCl) environment. On LPR test results shown in the figure 2, the polarization resistant (Rp) varies over time for the steel embedded in concrete, each point on the curve represents the average value obtained from three measurements. Previous studies on uncoated steel have demonstrated their properties against corrosion of alkali-activated steel slag (GBFS)

Test results in the first 3 months of study have found that a polarization resistance (Rp) in galvanized coating on reinforcing has much better result than galvanized uncoating on reinforcing structure, however some material can provide barrier protection allowing that the steel passive layers could be controlled. This condition could be improved on galvanic steel for the relationship between salt water-cement GBFS ratio, were high pH could be generate in the interface between steel and concrete and additional the passive layer exhibit good stability characteristics.

The evaluations at six-month exposure have shown that the chemical reactions between the steel and the cement hydration products reduce, the same way the Polarization resistance (Rp) values also, as shown in the figure 2.

Once metal reaching a metastable potential such that the Polarization resistance (Rp) becomes lower value in galvanic steel material. Premature failure of reinforced concrete structures occurs primarily due marine environments, because local acidification leading to localized corrosion.

Chloride penetration under these conditions occurs provided sufficient oxygen and moisture necessary, and then steel corrosion can take place. Chloride ions may penetrate the concrete through the pores and may cause serious decay processes, the type, amount, size, shape, and distribution of intragranular porosity may support attack on steel. Protective performance of steel bar embedded in an alkali-activated slag (AAS) concrete was considered in the evaluation and completed after study 6 months. The investigators found that during the 6 months corrosion test has a good set of conditions to generate resistant to corrosion [18]. The zinc serves as a sacrificial anode. Thus, if the two metals are electrically connected, corrosion of the zinc becomes a source of negative charge, which prevents corrosion of the steel. A coating thickness is within the range of from 100 microns, therefore acts as corrosion inhibitors. However, Due to the high alkalinity of pore water *(*pH 12.5–14*) in* concrete, the polarization should be reduced, this is because Zn is in this state actively. Rate values were computed from polarization resistance after 9 and 12 months and it was found that the (Rp) value increase, This is because drops on pH values close to 11, Then, thin layer of oxide protects the underlying layers of the metal and prevents the steel being attacked by chloride ions.

3.2 Electrochemical Impedance Spectroscopy (EIS)

Studies have established the benefits of using electrochemical monitoring techniques to learn about the electrochemical properties of steel embedded in concrete, due that the areas involved in Concrete Deterioration by Corrosion can be easily identified.

The principle involved in this technique is essentially measurement of the corrosion process of steel in concrete for every condition and materials, using circuit concept and modeling Equivalent Circuit process Modeling. The electronic unit consists of separate elements that represents the properties and processes of materials under test. It is worth noting that in the case of concrete pore solutions steel the electrochemical process in which metal reacts are a very complicated process, due to its intrinsic irregular morphology and chemical composition of concrete

Figure 3 shows typical Nyquist plots for uncouted steel rebars embedded in concrete, a decrease in all electrochemical parameters is obtained; especially the solution resistance and polarization resistance, in income levels tested result in higher (lower) demand for chloride ion in to concrete Nyquist plots observed that the phenomenon is similar for other levels studied in which a reduction is due to the leftward shift in all plots. A system is commonly represented by the circuit as shown in figure 4, which is the same as proposed by Assouli [19], explain the effect of action of chloride ion on the structural steel in equivalent circuits of corroding steel electrodes. In this study the best-fit model was selected using a resistance of an ionic solution in opposite value of the ionic concentration. This value is small in side of concrete because it can contain small amounts of chloride ions at the steel level. The saturation index is then determined based on level position, in the followings levels concretes are saturated of chloride solution and they are extremely aggressive then, resistance to ionic solution could be high.

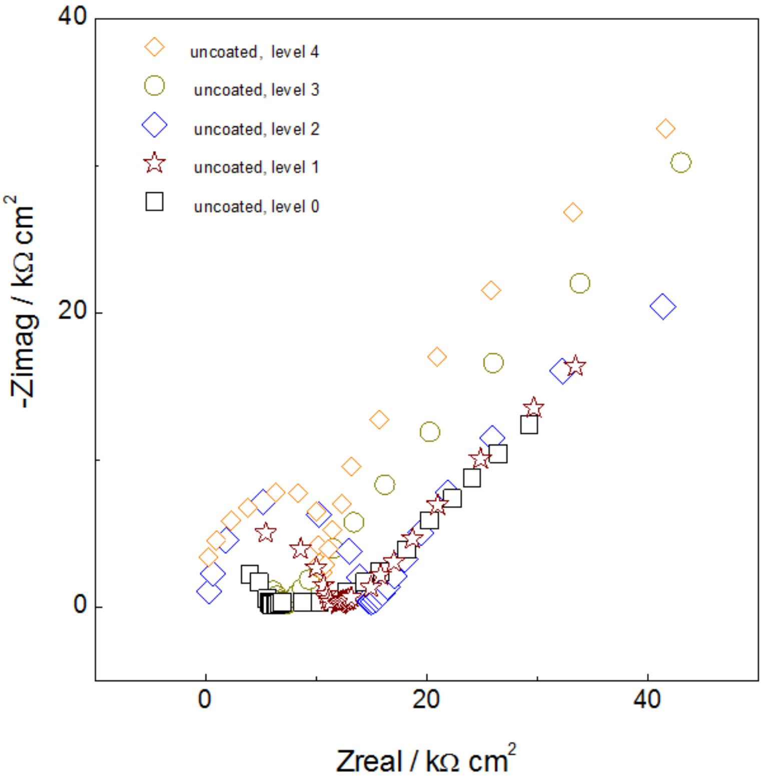

Figure 3. Nyquist plot that assesses the evolution of the electrochemical behavior of uncoated steel; embedded in the concrete of alkali activation.

The value of the resistor R1, which has been linked to reactions create a newly interface of Concrete and aggregates (stone or gravel and sand). Because resistance acts as a negative feed- back of the evaluated level,at the first level there are a best resistance to chloride ions Depending on the amount of chlorides present in the aggregates. Resistance of concrete to chloride ion penetration reduce depends the amount of chloride ions present. In this interface, constant phase elements CPE_1 are in parallel with R_1. CPE_1 acts as condensers of corrosion deposits and other imperfections found in the interface. The value of CPE_2 for test results is high because the ions generates other way which is represented by the resistance found between concrete and steel passivating layer, the value of the polarization resistance (R_2) is decreasing because the opposition in the early levels is higher due to the passivation layer found in this system this layer begins to be compromised after a certain amount chlorine ions have entered in the interface ,that means, as chlorine percent is increased by this interface; because of this the value of polarization resistance is decreasing, that indicate an increase in the corrosion rate, the constant phase element corresponding to this interface which is parallel to the polarization resistance shows a drop of this parameter this phenomenon is to be expected in this case because this element at each level offers greater passage of ions due to the deterioration that takes on the steel surface.

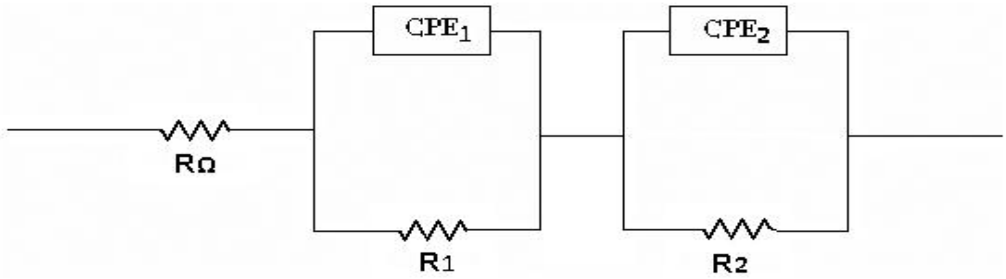

Figure 4. Equivalent circuit representing the behavior of uncoated steel embedded in concrete alkali activated slag with exposure to chloride.

In Figure 5, the behavior of coated steel is observed with galvanized embedded in the concrete, exposed to chloride solution. This system shows a behavior where the items found show a higher value in each of the levels examined, compared to uncoated steel, this is because the passivation layer is regenerating forming again generating a new protection against corrosive phenomena, this is also because the solution initially destabilized the protective layer due to reactions is not harmful for does not contain chlorine, corrosive agent in concrete.

The equivalent circuit used to simulate, what is happening in the system under chloride ion is similar to that proposed by Assouli [19], which was added to this circuit in concrete steel interface is a Warburg resistance (Figure 6). The resistance is an electrochemical element and describes impedance semi- infinite linear diffusion , this element is placed in this position because all Nyquist curves show an elevation on the x axis proportional to 45, in this material is observed that the resistance pore, resistance interface concrete-solution shows a small value for the first level , because this material has small chlorine content , then on the second level this value takes a high value because the material is already saturated with this solution therefore, this element creates a blockage to the passage of these ions , the value of this parameter is still maintained until the end of the measurements.

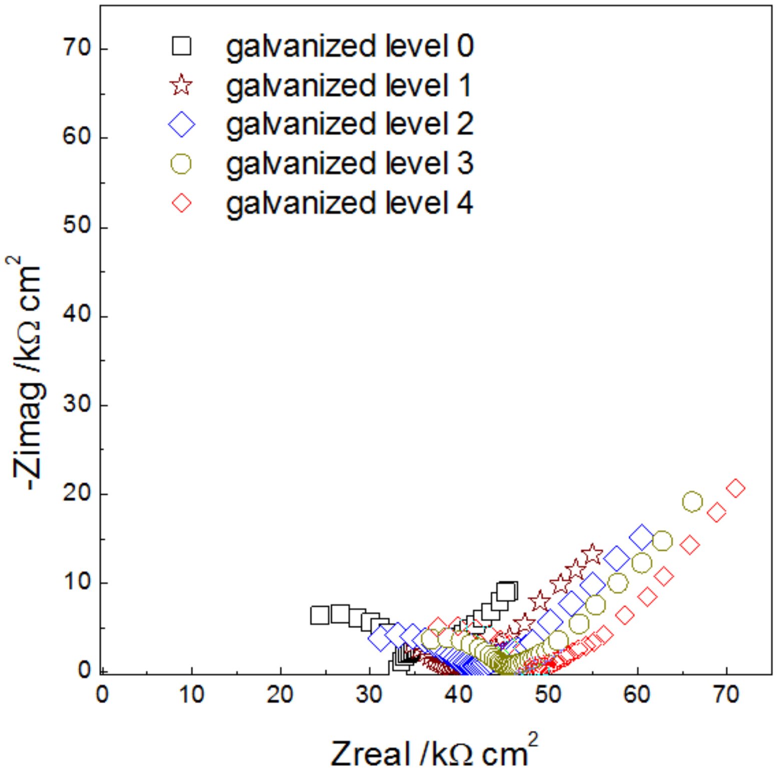

Figure 5. Nyquist plot corresponding to systems where the steel is covered with zinc; and embedded in the alkali-activated slag concrete. With increasing level of assessment, electrochemical parameters generate greater protection

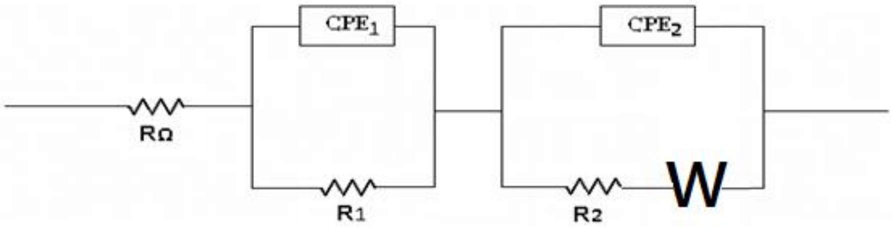

Figure 6. Circuit used for fitting, the electrochemical behavior of zinc coated steel and embedded in concrete alternative.

The resistance value is called shrinking Rpo because this interface generates -agregados solution reactions leading to some obstructing less aggressive in ion entry in the concrete- steel interface resistance is known in which each RCOR case becomes smaller because the passivation layer has already been destroyed passivation layer and is a direct means for engaging the steel , the last element found is the resistance of Warburg which is located on the steel is attacked in each level of chlorine ions so , therefore this value of this component decreases according to the level evaluation.

The value of the Rpo resistance is lower because the solution - aggregate interface generates some reactions that result in less obstruction in income of aggressive ion. In the concrete- steel interface, which the resistance Rcor in each case becomes smaller because the passivation layer has already been destroyed and is a direct way to affect the steel, the last item found, is the Warburg resistance which is located on the steel , it is attacked at each level by chlorine ions , hence the value of this component decreases according to the level evaluation.

4. CONCLUSIONS

The electrochemical study of concrete reinforced with galvanized coated steel and in to chloride ion environments, shown by resistance to polarization test that this material is passive. Under exposure to chloride conditions, Rp is growing in each evaluated levels. A tendency to stabilize the value of Rp in concrete having embedded uncoated steel is also observed. This could indicate that the final test in both cases has generated a stable passive film.

To determine the polarization resistance by the LPR method we were able to study the behavior of the concrete-steel system. The test considered that the greatest contribution to the ohmic resistance is generated by the solution pore concrete and not include the contribution of ceramic material, therefore the system is studied as a complete liquid electrolyte (pore solution) and rebar steel.

By using EIS technique, concrete - coated steel electrochemical system was obtained and is a little more complex than that provided by a Randles model, which consists of an additional Warburg element, with these considerations electrochemical equivalent circuit for the process has been established in each material.

Spectroscopy technique is also an electrochemical tool to study large number of interfaces, it can be determined with both the behavior of systems components (resistors, capacitors, constant phase elements, etc.) of each of them, and as system values or cell assembly (Rp, equivalent circuit) by this way, the test can be analyzed from several points of view , providing complementary information system studied in this specific case the concrete - steel reinforcement system coated galvanized .

ACKNOWLEDGMENT
This research was supported by "Vicerrectoría de investigaciones de la Universidad Militar Nueva Granada" under contract ING 1572.

References

1. F. Tang, G. Chen, J. S. Volz, R. K. Brow, M. L. Koenigstein, *Cem. Concr. Compos.*, 35 (2013) 171
2. A. A. Shah, Y. Ribakov, *Mater. Des*, 32 (2011) 4122
3. S. Fajardo, D.M. Bastidas, M. Criado, J.M. Bastidas, Electrochim. Acta, 129 (2014) 160
4. Q. Jiang, Q. Miao, W.-p. Liang, F. Ying, F. Tong, Y.i Xu, B.-L. Ren, Z.-J. Yao, P.-Z. Zhang, *Electrochim. Acta*, 115 (2014) 644
5. M. Criado, C. Monticelli, S. Fajardo, D. Gelli, V. Grassi, J.M. Bastidas, *Constr. Build. Mater*, 35(2012) 30

6. B. Liu, X. Z., G.-Y Xiao, Y-P Lu, *Mater. Sci. Eng., C*, 47 (2015) 97
7. I. Gurrappa, *J. Mater. Process. Technol*, 166 (2005) 256
8. C. C. Ryerson, *Cold Reg. Sci. Technol*, 65 (2011) 97
9. D. A Wicks, Z. W Wicks Jr, *Prog. Org. Coat*, 41 (2001) 1
10. R.R Roesler, K Danielmeier, *Prog. Org. Coat*, 50 (2004) 1-27
11. J. A Gonzalez, A. Cobo, M.N Gonzalez, S. Feliu, *Corros. Sci*, 43 (2001) 611
12. J. Cairns, Y. Duy, D. Law, *Constr. Build. Mater*, 22 (2007) 190
13. J. A. González, S. Feliú, P. Rodríguez, E. Ramírez, C. Alonso, C. Andrade, *Mater. Struct*, 29 (1996) 40
14. J. Newton, J. Sykes, J.M. *Corros. Sci*, 28 (1989) 1051
15. R. D. Brownea, R. Blundell, *Nucl. Eng. Des*. 3 (1972) 429
16. N. Hackerman, *Langmuir*, 3 (1987) 922.
17. R. Torres -Gomez, W. Aperador, E. Vera, R. Mejia de Gutierrez, C. Ortiz. *Dyna*, 164 (2010) 52.
18. D. A Koleva, J. Hu, A. L.A Fraaij, P. Stroeven, N. Boshkov, J. H W. De Wit, *Corros. Sci*, 48 (2006) 4001
19. B. Assouli, F. Simescu, G. Debicki, H. Idrissi, *NDT&E International*, 10 (2005) 682