

Corrosion behavior of galvanized steel in an atmosphere containing chlorides and sulfates by electrochemical techniques

Corrosión de acero galvanizado en un ambiente que contiene cloruros y sulfatos mediante técnicas electroquímicas

Received: 23- 04 - 2015 Accepted: 09-10-2015

Darío Yesid Peña Ballesteros¹
Anderson Sandoval Amador²
Hugo Armando Estupiñán Durán³
Deisy Sierra Fajardo⁴
Leidy Quintero Ascanio⁵



¹ Colombian, Engineering Metallurgical School and Materials Science PhD, Faculty of Physical-chemical Engineering, Corrosion Research. e-mail: dypena@uis.edu.co.

² Colombian, MSc Engineering School of Metallurgical Engineering and Material Science, Faculty of Physical-Chemical Engineering, Research Group in Corrosion. e-mail: anderson84f@gmail.com.

³ Colombian, PhD Department of Materials and Minerals Mine Faculty, Universidad Nacional de Colombia, Head Medellín, Group of tribology and e-mail: haestupinand@unal.edu.co

⁴ Colombian, Metallurgical Engineer, Metallurgical School PhD and Materials Science, Faculty of Physical-Chemical Engineering, Research Group in Corrosion. e-mail: deca1786@hotmail.com.

⁵ Colombian, Metallurgic Engineer, School of Metallurgical Engineering and Materials Science, Escuela de Ingeniería Metalúrgica y Ciencia de Materiales, Faculty of Physical-Chemical Engineering, Research Group in Corrosion. e-mail: lemaquias_1@hotmail.com.

Abstract

It was studied Corrosion behavior on galvanized steel sheets, immersed in solutions with different concentrations of NaCl and Na₂SO. The steel sheets were immersed using an elevator, in order to simulate an atmosphere, wherein the sheets were always interacting with corrosive medium. The degradation was evaluated by electrochemical impedance spectroscopy and potentiodynamic curves. The morphology of surface was analyzed by scanning electron

Microscopy and the composition of the corrosion products was determined by EDX and XRD. The results after 30 days showed that the corrosion potential increased with the time, confirming the formation of passive products on the surface; corrosion rate also increased, causing pitting corrosion. For the first few days of exposure, generalized corrosion was observed as a result of compounds passive, porous nature and white.

Key Words: Atmospheric corrosion; electrochemical test; galvanized steel.

Introduction

Galvanized is a coverage widely used in the industry. Zinc is a metal with a behavior more active than iron; however the life span of the coverage is major compared with the one of the naked iron, due to the formation of an oxide protective film over its surface. The galvanized steel exposed to tropical atmospheres, is affected by the action of agents present in the marine atmosphere, due to the relative humidity temperature and exposure time to the environment, which causes a change in the composition of

the protective layer, and thus a decrease in their resistance to corrosion. The enterprises producers of galvanized steel must confront themselves to this problem of corrosion, due to the fact that is inevitable the contact with corrosive agents and the humidity at the time of storage, where if it's even for a short period of time the humectation time upon the steel is enough to generate corrosion scopes, before its dispatching. This way, in these short periods of time the permanency of the electrolyte upon the steel, can begin an atmospheric corrosion.

The corrosion in galvanized steel is a very complex process that implies various electrochemical and physical mechanisms that generally are given in three different stages. According to studies of Dubuisson *et al.* (2006), in the first stage, the galvanized steel's electrochemical behavior relates itself with the dissolution in the zinc oxide layer that makes contact with the air. In the second stage, the zinc's surface covers itself with a white oxide that allows the corrosion of the steel. During this stage the corrosion speed of the zinc layer rapidly decreases, coupled with a potential change in corrosion to a more noble corrosion. In stage three, the galvanized steel's corrosion advances to steel dissolution, so, in this stage the zinc coating doesn't act anymore as a sacrifice anode.

Authors like Padilla & Alfantazi (2014) & Hamaloui (2008), have employed the electrochemical techniques to study the behavior against the corrosion of galvanized steel, simulating environmental conditions with chlorides and sulfates, finding that the potential-dynamic tests and spectroscopy of electro-chemical impedance tests, are a fundamental tool to discern, which of the absorbed species over the zinc surface, are the responsible in forming the corrosion products. In this train of thoughts, a study is necessary of the behavior of the galvanized steel before atmospheric corrosion through established electro-chemical techniques, simulating environmental conditions.

Methodology

It was made an experimental design with the goal to quantify the number of tests and necessary repetitions. Manipulative variables were taken in account, the concentrations of sodium chloride and sodium sulfate, and the staying time of the foils. Charts 1 and 2.

In this stage the test tubes were suited to a 30*30 mm size and the edges were protected with an Acorlad P1 duct tape to avoid the localized corrosion.

Chart 1. Variables utilized. Chloride and sulfates concentration [g/400ml].

Variable	Type	Values		
[Cl ⁻]	Variant	4.33	9.74	15.15
[SO ₄ ⁻²]	Variant	5.36	10.72	16.08
Time (days)	Variant	0	15	30

Source: The authors

Chart 2. Used solutions

	[Cl ⁻] g/400 ml	[SO ₄ ⁻²] g/400 ml	[Cl ⁻] M	[SO ₄ ⁻²] M
1	4.33	5.36	0.18	0.09
2	15.15	5.36	0.64	0.09
3	4.33	16.08	0.18	0.28
4	15.15	16.08	0.64	0.28
5	9.74	10.72	0.42	0.18
6	9.74	-	0.42	-
7	-	10.72	-	0.18
8	-	-	-	-

Source: The authors

Superficial characterization of the galvanized

Micrographies were takes through an Olympus BX-41 microscope and a SEM was done. The specifications of the study of galvanized steel foil are shown in Chart 3 and 4; were C: Coverage and F:Foil.

Chart 3. Coverage designation

JIS G3302	ASTM A653	NTC 4011
Z75	G90	Z275

Chart 4. Specific study foil

Thickener [mm]	Dimensión [mm]	Weight R [g/m ²]	Thickener R [mm]	Weight L. [Kg]
3.0	1220*2440	257	0.038	70.37

Source: Technical manual of galvanized steel

A mechanic elevator was design for the test tubes to be submerged and be submerged in the solution every 12 hours during 15 and 30 days, to allow the presence of atmospheric corrosion.

Electro-chemical tests

In the assembly of the electro-chemical cell it was done under the ASTM G109 (ASTM INTERNACIONAL,

2003) standard were it was used; a reference electrode Ag/AgCl, against a graphite electrode, as a work electrode a sample of galvanized steel was used (1). The electrochemical tests were done in a GAMRY 750 potentiostat.

Microscopy tests

With the goal to know the superficial change that was observed in the test tubes at the end of the corresponding days to each one of them, electronic microscopy sweeping tests were done, dispersive energy spectrometric and rays diffraction. The electronic microscopy was done in an electronic field emission field sweeping microscope (Fesem) from Quanta® FEG 650 FEI in 10 kV equipped with a large field detector (*Large Field Detector*, LFD). The elemental analysis in 10 kV, was done with an Energy dispersive X-Ray spectroscopy add-on (EDX). The chemical analysis was made with a Leo 1550 Fesem equipment at 20 kV, it was done with an EDX. The samples analysis by DRX used in a diffractometer of X-Rays brand BrukerR model D8 Discover with Geometria Davinci using radiation CuK α 1= 1.5406 Å°.

Results and results analysis

Superficial analysis of the galvanized steel

In the Figure 1 is shown that the morphology of the galvanized steel in its delivery state is homogeneous and its crystallographic orientations are determined by each grain; darker zones than others have been observed, due to the light diffraction through the crystal. To greater magnifying pores were observed through the whole surface, Figure 1b, condition which helped the electrolyte-coverage diffusion process, and this takes to the oxidation of the galvanized with ease. On other hand, the figures 1c and 1d, show the Micrograph in the study point where the elemental analysis was made from the same and the EDX results, respectively.

Finishing the 15 days of exposition, Figure, 2, the morphology of the coverage is heterogeneous with the preferential zones (ASTM INTERNACIONAL, 2003). The surface's texture presented plain and disorganized crystals, due to the formation of products like simonkoleita that was characterized for being of protective and porous nature. The simonkoleita, is formed after the formation of hydrozincite, being both white color products (Seré *et al.*, 1997). In other zones it was observed the presence of smaller crystals

whose massive form and non-homogeneous growth covers major surface area. This takes to a generalized corrosion in all of the surfaces of the test tube.

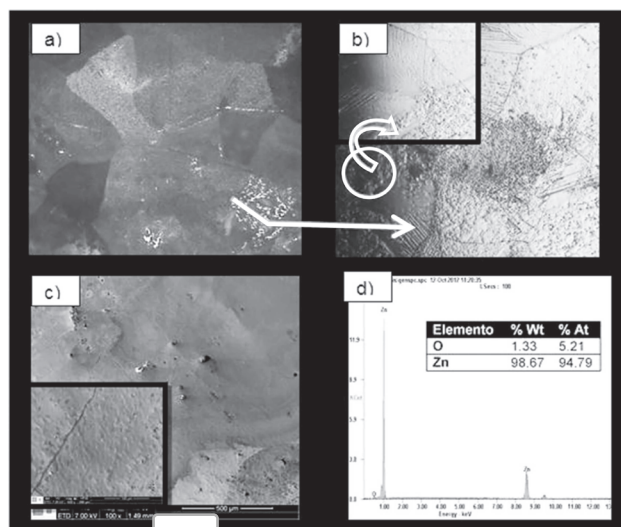


Figure 1. Micrograph in the delivery state, without magnifying; b) Optic Micrograph at 10x and 50x; c) SEMA Micrograph at 100x; d) Analyzed EDX sample. **Source:** The authors

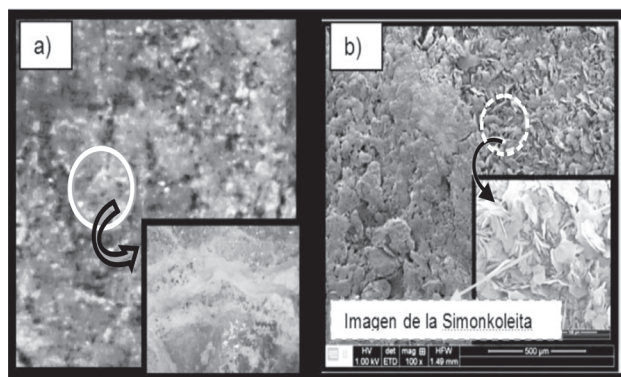


Figure 2. Micrograph solution 5 (15 days), a Micrograph SEM, without magnifying and at 10x. b) Micrograph at 100x and 500x **Source:** UIS Microscopy laboratory

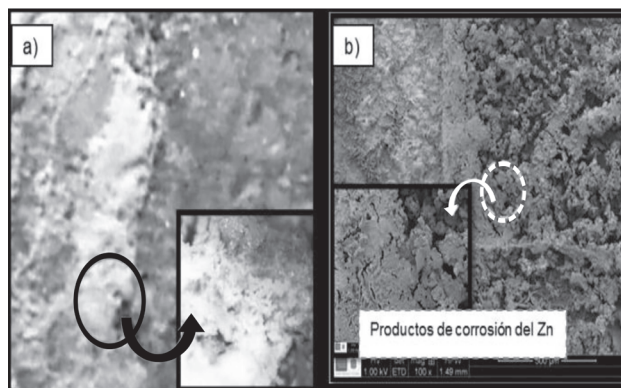


Figure 3. Micrograph solution 2 (30 days). a) Micrograph SEM, without magnifying and at 10x. b) SEM micrograph at 100x and 500x. **Source:** UIS Microscopy laboratory

The Figure 3, shows the solution 2, after 30 days, the plain crystals disappeared and the massive product grew giving place to a formation of small islands. Situation associated to the continuous process of oxidation by the part of the already formed products and to the carbonate ions exchange for chloride ions for the formation of soluble salts. This takes to a localized harm and finally at the mincing of the test tube. By such reason, composites like steel chloride were found, indicating that the corrosion process has reached the base metal (Hernández *et al.*, 2011).

To verify the presence of formed corrosion products in the galvanized steel samples that were exposed to atmospheric corrosion for a time of 15 and 30 days, in the 5 and 2 solutions respectively, and EDX was held, for the elemental analysis, Figures 4, 5 and 6. In these, it is observed at 30 days the presence of Fe different to the 15 day EDX, which means that the steel is possibly exposed to this exposing time.

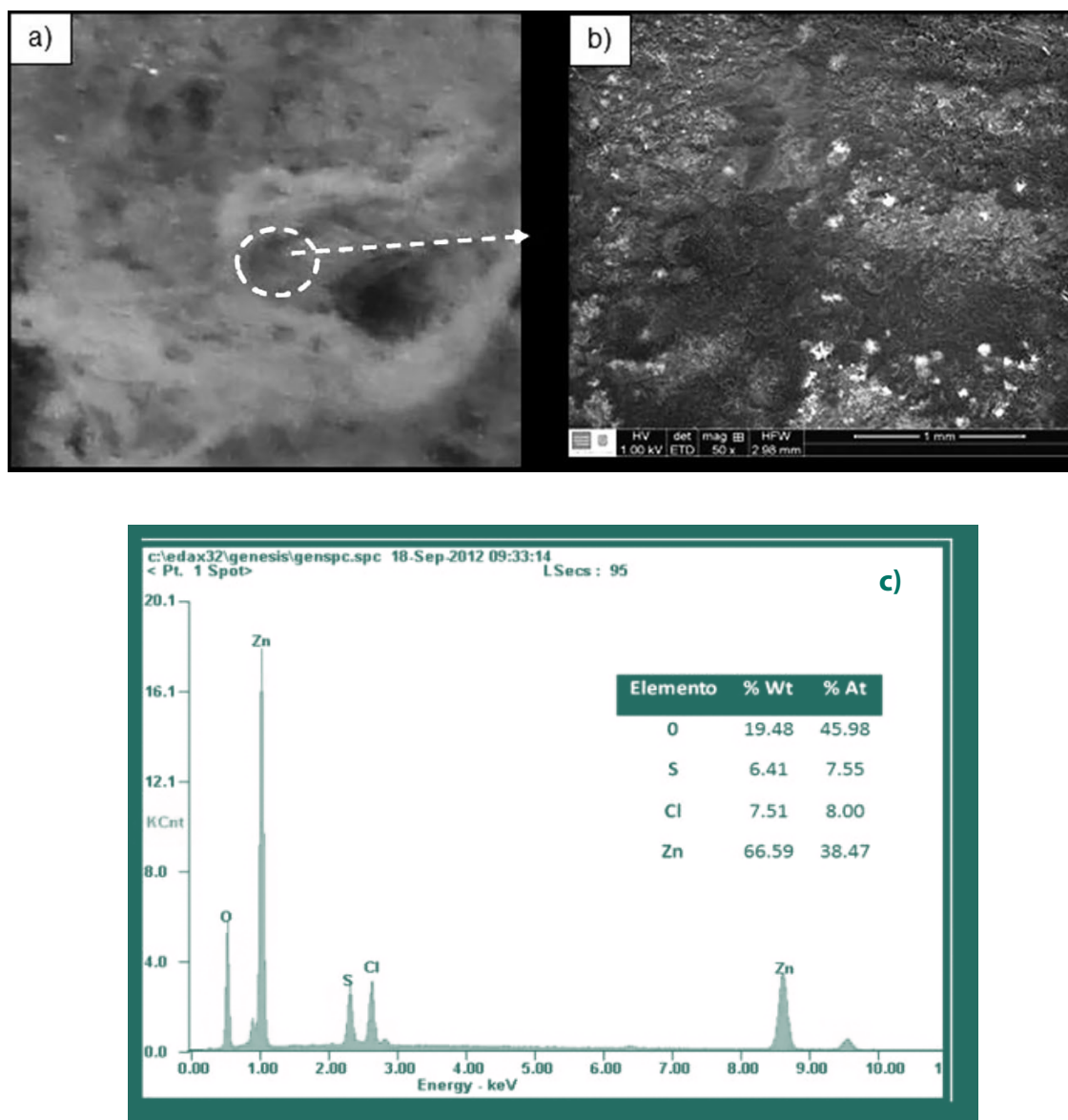


Figure 4. Micrograph of the analysis's study zone of the submerged test tube in the solution 5 (15 days), a) image without b) Micrograph at 50x, c) Respective EDX.

Source: UIS Microscopy Laboratory

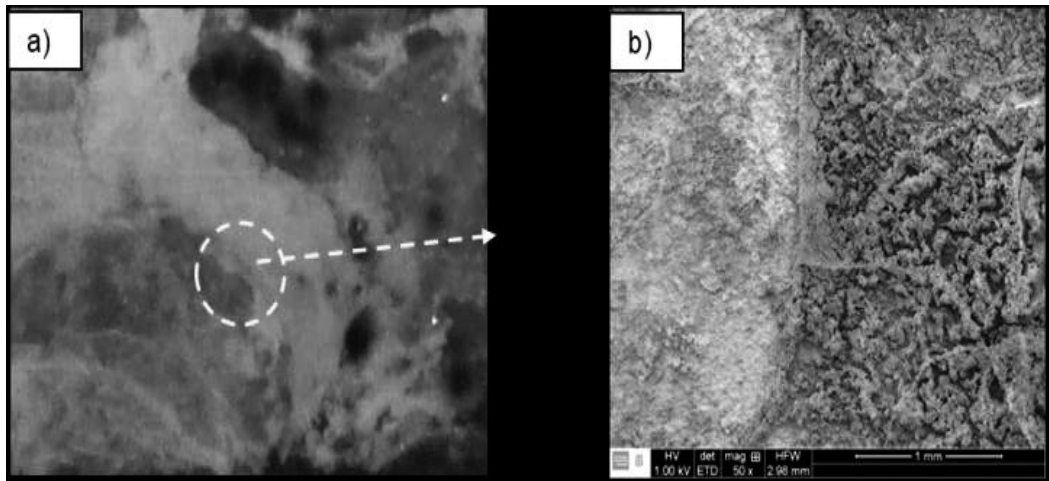


Figure 5. Micrograph de la zona de estudio de la probeta sumergida en la solución 2.
 a) Imagen sin aumento, b) Micrograph a 50x.
Source: Laboratorio Microscopia UIS

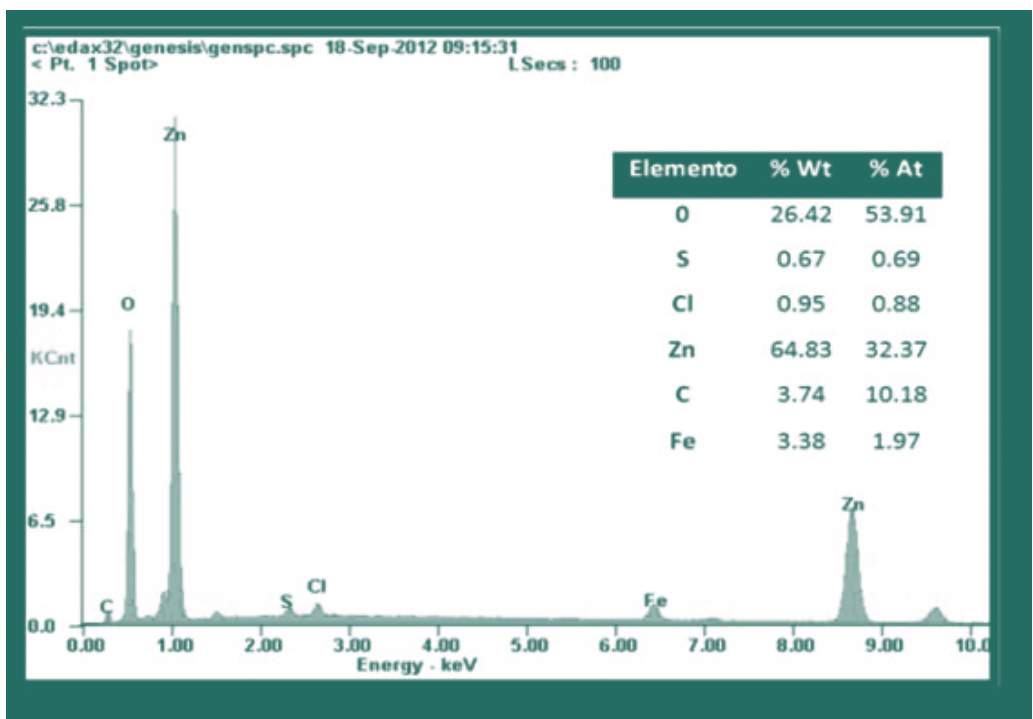


Figure 6. EDX of the test tube submerged in solution 2.
Source: UIS Microscopy Laboratory

The results of the X-rays diffractions were done based in two specific solutions: the solution 2 which concentration of chlorides was bigger than the sulfates and ended in a 30 day time, and the solution 5 that finished its exposition to 15 days. To know the products of corrosion that were formed in these times that the X-ray diffraction test was

done, obtaining the next results, shown in chart 5 and Figure 7a and 7b.

It is observed the presence of corrosion products related steel with the steel's iron at the 30 day exposure and unstable iron oxide (magnetite).



Chart 5. Crystalline stages present in the solutions.

15 DAYS OF SOLUTION 5 EXPOSITION	
Crystalline stages	Name
$NaZn_4(SO_4)Cl(OH)_6 \cdot 6H_2O$	Gordaita
$(Na_{0.8}Zn_{0.1})_2SO_4$	Zinc and sodium sulfate
$Zn_5(OH)_8Cl_2(H_2O)$	Simonkolleita
30 DAYS OF SOLUTION 2 EXPOSITION	
$NaZn_4(SO_4)Cl(OH)_6 \cdot 6H_2O$	Gordaita
$NaCl$	Halita
$Zn_5(OH)_8Cl_2(H_2O)$	Simonkolleita
$FeCl_2$	Steel chloride
$ZnSO_3 \cdot 2.5H_2O$	Hydrated Zinc sulfite
Fe	Steel
$Fe_{2.962}O_4$	Magnetite

Source: The authors

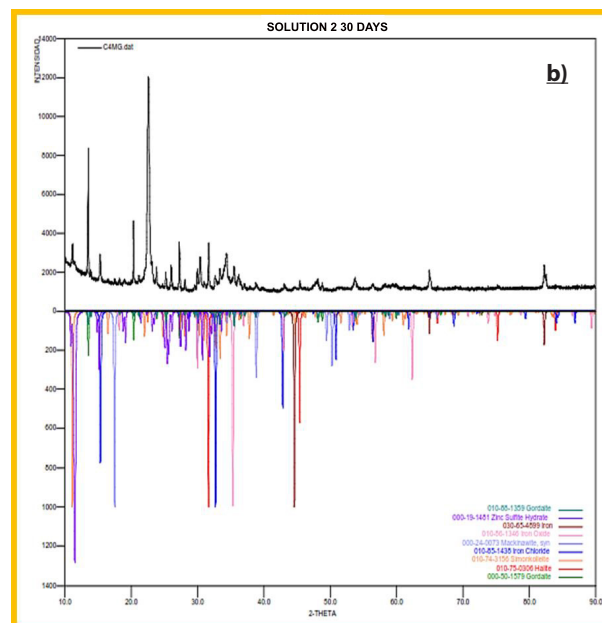
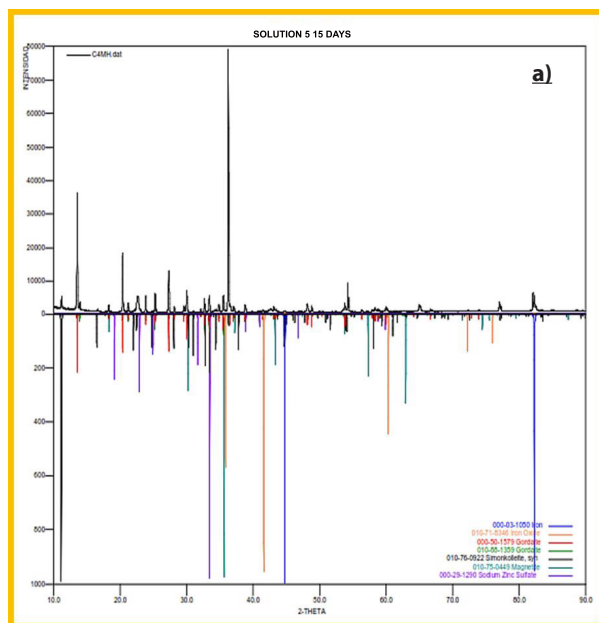


Figure 7. DRX of the submerged test tubes for 15 and 30 days

Source: The authors

Electrochemical spectroscopic impedance

When analyzing the diagrams of impedance it was observed the appearance of two inflexion points, Figure 8, showing that there are two time constants (the slopes are negative) in the corrosion reactions. The first at low frequency, is related with the resistance to the mass transference, which is major to 0 than to 30 days. To higher frequencies, the charge transference is major to 30 days of exposition than to 0 days which is related to the formation of corrosion products that degrade zinc with the possible exposition and steel degradation in solution that proves the observed in the DRX analysis.

Information is presented from two semicircles, which can identify the Nyquist diagram at 0 immersion days, Figure 9. The first semicircle is formed at high frequencies and is attributed to the transference process of faradaic charge (Echeverría, 2002) and the second one is formed at intermediate frequencies due to the resistance that present the film to react (resistant to the zinc conversion or resistance to the mass transference); besides this semicircle ends with an inductive behavior related with the heterogeneous mechanism of adsorption at low frequencies from 0.03-1 Hz (the slope is positive in the Bode diagram) and has a phase angle that varies between 0° and -20°.

This behavior of the impedance was given for all the solutions at 0 days, with the exception of the solution 6 (without the presence of sulfate ions), whose Nyquist diagram doesn't present inductive behavior at low frequencies. The circuit equivalent proposed by adjust of the experimental data is shown in the Figure 10.

When the solutions were submerged during 15 and 30 days according to the respective concentration of chlorides and sulfates, the impedance of the system kept showing two constants of time but none with inductance, it is possible that this occurs due to the effect of a decrease in the electro-chemical diminution of dissolved solid in the solution and the attached products to the test tube's surface, which avoids the adsorption at low frequencies.

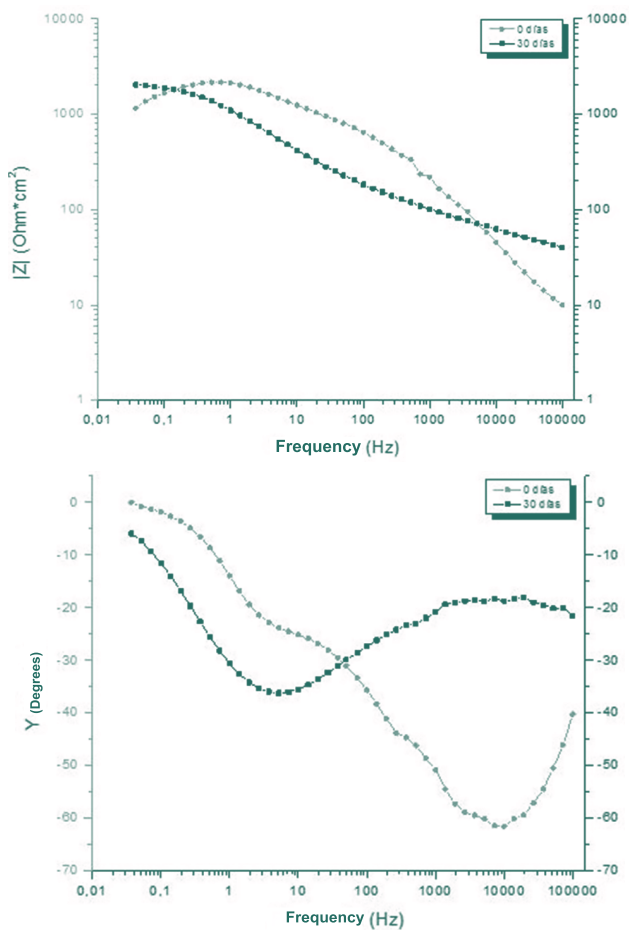


Figure 8. Bode diagram for the solution 2 at 0 and 30 of immersion.

Source: The authors

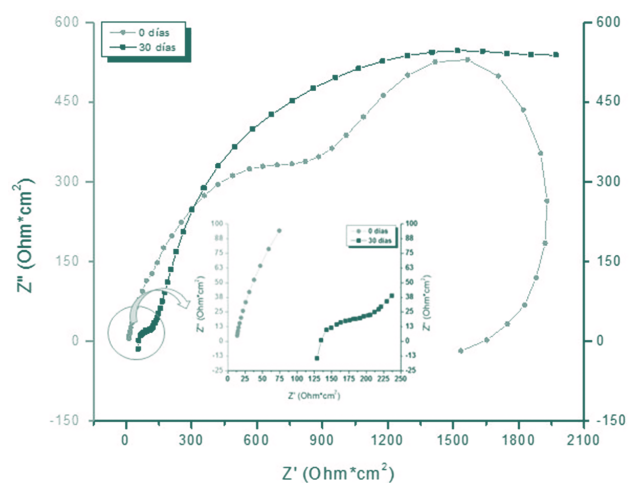


Figure 9. Nyquist diagram for the solution 2 at different immersion times.

Source: The authors

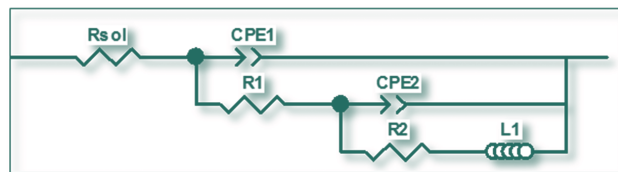


Figure 10. Circuit equivalent for the solutions at 0 days
Source: The authors

For 15 days (solution 5) the resistance to the charge transference increased considerably respecting to zero days and this takes decrease in the ionic conductivity and in the corrosion ed, evidence in the Figure 11, where is shown that the curve moves towards more positive potentials, that means it moves away from the active zone, and the corrosion density decreased because the galvanized reacted with the solution forming corrosion products $Zn(OH)_2$ and $ZnCO_3$, when attaching to the surface and forming a form layer (generalized). This caused a decrease in speed corrosion that also was observed in the resistance to polarization curve, Figure 12, where R_p 's value for 15 days is greater than in 0 days.

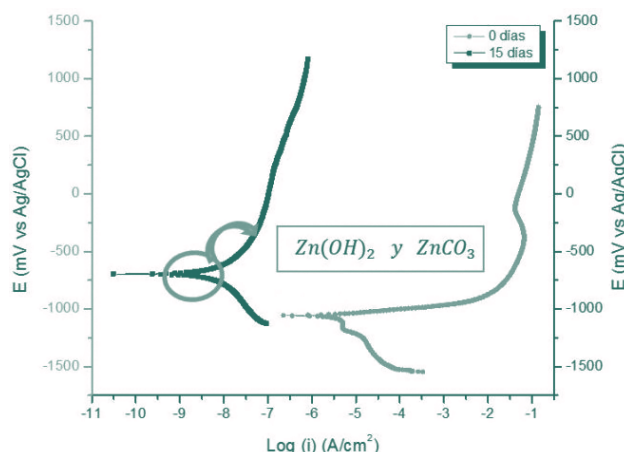


Figure 11. Potential-dynamic curve for the solution 5.

According to these results, corrosion for a time of 30 will depend of the concentration of aggressive ions present in the solution, of the corrosion products characteristics that can be forming with time (adherence and porosity) and superficial condition (zinc) of the test tube. An increase in the potential corrosion observed in the potential-dynamic for the solution 2 and 5 in a decrease of the density in the corrosion stream with the exposition time, it has been observed, probably due to the concentration of chlorites was higher than the concentration of sulfates, Figure 13. (INTERNACIONAL, 2010; INTERNATIONAL, 2010; Yadav *et al.*, 2004a; Arenas and Damborenea, 2006).

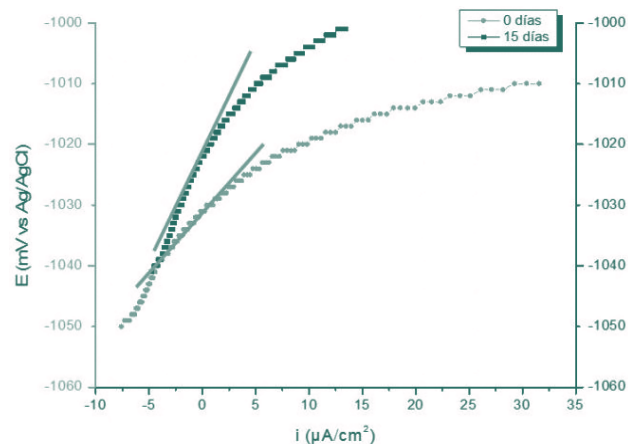


Figure 12. Resistance curve in the lineal polarization for solution 5.
Source: The authors

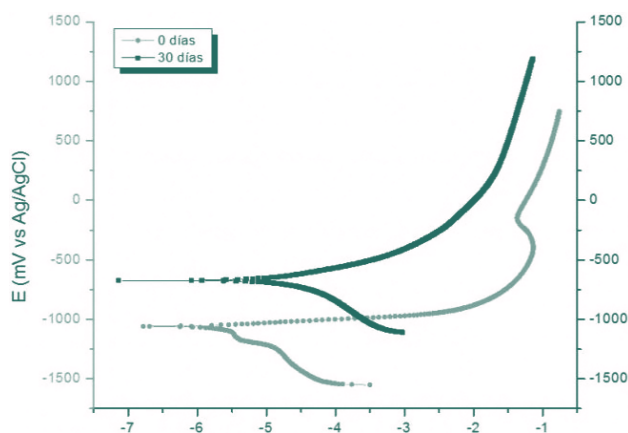


Figure 13. Potential-dynamic of solution 2.
Source: The authors

It is worth to mention, that for a solution where are present the chloride sulfate, a high concentration of the last makes the increase in corrosion whether it's 2 or 3 times higher regarding the increase by the effect of chlorides. (Yadav *et al.*, 2004b; Arias, 2011).

Conclusions

- The corrosio ed of the system exposed to chlorides and sulfates, presented a time reduction for a time of immersion-emersion of 15 days in the solution 5, due to that the galvanized-electrolyte interphase made itself more resistive as it was observed in the Nyquist curve and the values of the phase angle, who tend to zero; however increased when finishing the 30 days of study, which was verified in the potential-dynamic curve, which moved itself towards higher values in the stream density, evidencing a

higher steel exposition to the solution (no protection of the galvanized).

- The galvanized steel presented generalized corrosion for the first days of exposition, influenced by the polluting ion concentration in each solution; and for the 30 days it presented localized type damage (with sting points) on its surface.

- Due to the variations of the impedance regarding the exposition time, two equivalent circuits were proposed one for 15 days and another for 30 days where resistance to the solution and two time constants; and another for 0 days where additionally the already proposed circuit, it includes and inductor due to the adsorption of chloride and sulfate ions in the interphase electrolyte-covering.

Galvanized steel foils that in its storage stage are exposed to environments that contain chlorides and sulfates, for a time less than 15 days, have a good protection against corrosion, due to the high resistance of formed products.

References

Arenas, M. A., and Damborenea, J. J. (2006). Mecanismo de corrosión e inhibición electroquímica del acero galvanorecocado . *Revista Metalurgia* , 165 - 174.

Arias, A. C. (2011). *Estudio del comportamiento de un ambiente corrosivo con cloruros y sulfatos, sobre una lámina de acero galvanizado*. Universidad Industrial de Santander, Bucaramanga: Trabajo de grado.

ASTM INTERNACIONAL. (2003). Standard test method for determining effects of chemical admixtures on corrosion of embedded steel reinforcement in concrete exposed to chloride environments. *ASTM G*, 97 - 109.

ASTM INTERNATIONAL. (2010). Standard practice for calculation of corrosion rates and related information from electrochemical measurements. *ASTM G 102* - 89.

Echeverría, C. A. (18 de Septiembre de 2002). *Monografías: Corrosión atmosférica del acero en condiciones climáticas de Cuba. Influencia del aerosol marino*. Recuperado de: [umcc.cu/monos/2002/ Carlos%20Echeverria.pfd](http://umcc.cu/monos/2002/Carlos%20Echeverria.pfd).

Hernández, L., Hernández, L., and Rodriguez, S. (Sem de 2011). Recubrimientos para aumentar la duración del acero galvanizado. *Memorias del XVII congreso internacional anual de la somim* (págs. 749 - 755). San Luis Potosí: SOMIM.

INTERNACIONAL, A. (2010). Standard practice for conventions applicable to electrochemical measurements in corrosion testing. *ASTM G3* - 89.

INTERNACIONAL, A. (2010). Standard test method for conducting potentiodynamic polarización resistance measurements. *ASTM G59* - 97.

Seré, P. R., Culcasi, J. D., Elsner, A. R., and Sarli, D. (1997). Factores que afectan a la temperatura de los recubrimientos de cinc obtenido por inmersión. *Revista de Metalurgia.*, 376 - 381.

Yadav, A. P., Nishikata, A., and Tsuru, T. (2004). Degradation mechanism of galvanized steel in wet-dry cyclic environment containing chloride ions. *Corrosion Science*, 165 - 174.

Yadav, A. P., Nishikata, A., and Tsuru, T. (2004). Electrochemical impedance study on galvanized steel corrosion under cyclic wet - dry conditions - influence of time of wetness. *Corrosion Science*, 169 - 181.