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Effect of Chloride Ions on the Corrosion of Galvanized Steel Embedded in Concrete Prepared with Cements of Different Composition

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The behavior of galvanized steel inside concrete prepared with different types of cement is of vital importance in the latest construction mega-projects, which demand durability in environments as aggressive as sea water. This paper presents the results of a year of study on the behavior of galvanized steel rebars against the action of chloride ions. The steel bars in question were used in reinforced concrete prepared with Standard Portland cement and Pozzolanic cement at a water/cement ratio of 0.45, and then exposed to a 2.6 M NaCl solution with cycles of 4 days semi-immersion and 3 days drying at 60ºC. The state of the galvanized steel bars was monitored through measurement of corrosion potential and corrosion current over time. Chloride ion entry profiles were also studied. The composition and morphology of the corrosion products formed on the galvanized steel were analyzed by MEB-EDAX. Polarization curves were used to evaluate the behavior of the galvanized steel bars in alkaline solutions; these bars were taken from concrete specimens exposed to an artificial marine media. It was shown that the behavior of the galvanized steel bars varies with the composition of the cement used depending on tricalcium aluminate content and its interaction with the chloride ions. In both types of concrete the galvanized steel bar was found to be in a passive state at the end of the test period.

Keywords: corrosion, concrete, galvanized steel, chloride.

1. INTRODUCTION

One of the biggest challenges of recent years has been to increase the useful life of reinforced concrete structures exposed to coastal areas. The problem of durability caused by premature deterioration of the reinforcing structure leads to high financial losses from the cost of necessary maintenance and repairs [1-4].

One factor that influences structure durability is the presence of aggressive agents, such as carbon dioxide (CO_2) and the chloride ion (Cl^-). CO_2 produces carbonation processes which decrease pH causing the layer of protective carbon steel oxides to break down, leading to widespread corrosion of the steel frame [5-7]. Chloride ions induce localized corrosion on carbon steel bars [8-16]. As a consequence, the carbon steel forms corrosion products that can reach a volume ten times that of the base steel [4,17], which are of low adherence and generate tensions that surpass the compressive strength of the steel frames, leading to the appearance of fissures or cracks, which in turn act as possible entry points for aggressive ions, exposing the structure to more accelerated corrosion processes.

For this reason, different authors have studied the best way to increase the useful life of reinforced concrete structures through, for example, the use of organic compounds such as epoxy resins [18], the addition of corrosion inhibitors [19], cathodic protection via impressed current [12,20] or hot-dip galvanization [21-31].

Hot-dip galvanization consists of coating the carbon steel with a layer of zinc by submerging it in a bath at 450-460ºC [3, 23, 25], thus giving the bar a protective barrier against aggressive ion attack. It also gives cathodic protection through sacrifice anode as the zinc is more anodic than the steel, thus increasing the chloride ion concentration threshold at which the steel frame would be at risk of severe corrosion. Zinc also possesses a greater range of pH stability than carbon steel, from 6 to 12.5, and therefore, it is able to resist drops in pH caused by carbonation of the concrete and the use of different types of cement which differ in type of aggregate and in the pH they give to the concrete. Zinc also generates less voluminous corrosion products than those formed by carbon steel, decreasing the probability of the appearance of cracks. Zn corrosion products are also more powdery and can therefore be dispersed through the system of pores on the metal/concrete interface, thus delaying the arrival of aggressive agents from the exterior of the concrete covering [1, 26].

Bouteiller [5] has studied concretes prepared from two types of cement, finding the threshold of chlorides needed to initiate corrosion of carbon steel and establishing that aggregates to Ordinary Portland cement improve the resistance of the steel to the change from passive to active, with differences in the behavior of the steel depending on the type of concrete. This study found that the aggregate used in Ordinary Portland cement improves resistance to the penetration of chlorides due to the transport properties over the ability to combine chlorides. They also found that the carbon steel frame begins to corrode with a concentration of free chlorides of 0.7% in cement weight, though they propose that instead of a critical chloride concentration value, it is more realistic to express a critical range of chloride ion concentration. In an earlier study, Vera et al. [26] showed the importance of concrete type and that in addition to free chloride ion concentration, the initiation of corrosion or the change from passive to active depends on the diffusion rate of the chlorides entering the concrete matrix and reaching the steel reinforcement.

In Chile the most commonly used types of cement are Ordinary Portland and Pozzolanic. The first of these is imported and natural pozzolans from the region are sometimes added to it to generate pozzolanic cement. The present study therefore aims to identify the influence of the two types of commercial cement used in the country, Ordinary Portland and Pozzolanic, with regard to the behavior of galvanized steel rebars embedded in concrete against the action of chloride ions, using non-destructive measurements of corrosion potential and corrosion current, as well as electrochemical analyses and SEM-EDX and DRX analysis of the corrosion products.

2. EXPERIMENTAL PROCEDURE

2.1. Specimens Design

The study was carried out using two types of cement, Ordinary Portland and Pozzolanic; their composition was provided by the suppliers and is shown in Table 1. The amounts used and the w/c ratio of 0.45 are shown in Table 2. The reinforced concrete specimens were cured in a wet chamber for 28 days at 25ºC and 90% humidity.

Table 1. Cement composition (%).

Cement type/Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
Ordinary Portland	21.3	4.9	3.4	65.4	0.1	0.85	0.5	2.5
Pozzolanic	21.5	4.6	3.3	62.0	2.7	0.2	0.4	2.2

Cement type/Compound	Mn_2O_3	P_2O_5	Free CaO	C_3S	C_2S	C_4AF	C_3A	Pozzo-lans
Ordinary Portland	-	-	-	55.0	30.0	9.0	12.0	-
Pozzolanic	0.08	0.09	0.5	45.0	20.0	12.0	7.0	29.7

For the analyzes cubic specimens were made. They measure 15 cm along each side and contain two galvanized steel bars at a depth of 3 cm into the concrete. The bars have a diameter of 3/8”, are 16 cm in length and their Zn coating is 80 µm thick. Prism-shaped specimens measuring 15 x 7 x 5 cm were also used in the quantification of chloride ions, while 5 cm cubic probes and 5 x 5 x 3 cm prisms were used for the physical characterization of the concrete. Mechanical properties were measured on the 15 cm cubic specimens.

Table 2. Concrete composition per m^3

Mixture	Cement (Kg)	Water (L)	Gravel (Kg)	Sand (Kg)
w/c : 0.45	425	191	1044	736

2.2. Chemical, physical and mechanical characteristics of the cement and concrete

In order to corroborate the composition of the cements, the components of the Ordinary Portland and Pozzolanic cements were characterized using DRX with an XPERT-PRO diffractometer.

Initial quantification of free chloride ions was also conducted. Portions of 15 g of powdered concrete were taken and dried at 105ºC for 24 hours, this was then stirred with deionized water for 3 hours and gravity filtered with Whatman Cat No 1005 – 110 filter paper. Aliquots of 25 ml were taken and evaluated in accordance with the Möhr Method. For each solution the initial pH was measured with a HANNA INSTRUMENTS glass membrane pH 210, Microprocessor pH Meter.

The mechanical and physical characterization of the concrete was carried out through compressive strength testing at 28 and 90 days in accordance with ASTM C 39, Resistivity in accordance with UNE standard 83988-1, Absorption and Total Porosity in accordance with ASTM C642-90 and Capillary Absorption in accordance with the Fagerlund Test.

2.3. Corrosion measures

An accelerated chloride ion exposure test was conducted using a 2.6 M NaCl solution. It was carried out in cycles of 4 days semi-immersion and 3 days drying at 60ºC. Corrosion potential was measured every two cycles using an open circuit for 30 minutes until stability was attained with a G-SC V 2.0 Potentiostate-galvaniostat, a $Cu/CuSO_4$ $_{(sat)}$ reference electrode and a copper counter electrode. Polarization resistance was measured under the same conditions with a sweep of ± 10 mV of the corrosion potential, while corrosion current was calculated in accordance with the Stern-Geary equation assuming a value of 26 mV/decade for the B constant.

2.4. Quantification of free chloride ions and pH measurement

Chlorides were quantified after 12, 24, 40 and 50 cycles at depths of 1, 2 and 3 cm, using the same procedure used for the quantification of initial free chlorides. pH was measured under the same conditions using a HANNA INSTRUMENTS glass membrane pH 210 Microprocessor pH Meter.

At cycle 50, the combined chlorides were quantified using acidic digestion of the concrete with concentrate nitric acid for a period of 30 minutes, followed by application of the Möhr Method.

2.5. Morphology and composition of the galvanized steel

The initial morphology and composition of the galvanized steel bars were analyzed along with the corrosion product formed after 50 cycles, using a CARL ZEIS EVO/MA/10 sweeping electron microscope coupled to an EDAX (SEM-EDS) and using X-ray diffraction with an XPERT-PRO diffractometer.

2.6. Polarization Curves

The behavior of the galvanized steel was studied in real pore solutions from concrete exposed to the prior corrosion tests; these solutions were prepared using crushed concrete dried at 105ºC for 24 hours, then stirred for 3 hours in deionized water and finally gravity filtered through Whatman Cat No

1005–110 filter paper. A saturated calomel reference electrode and a platinum counter electrode were used, while the galvanized steel bars were used as the working electrode after degreasing with acetone. The corrosion potential of the system was measured for 30 minutes and a sweep potential of -500 mV_{sce} to 2000 mV_{sce} over the corrosion potential, in the anodic direction, was used.

3. RESULTS AND DISCUSSION

3.1. Chemical, physical and mechanical characteristics of the concrete

The results of the X-ray diffraction analysis of the cement show higher calcium carbonate content, so-called limestone or limestone filler, in the Pozzolanic cement at 17.4%, in comparison with 11.8% in the Portland cement. This aggregate is used in certain types of cement as its small particle size leads to dense paste that fills the pores of the concrete [32-35]. It reacts with the C_3A in the cement, accelerating the process of hydration and decreasing the capacity of the concrete to react with chloride ions that enter its matrix, as shown by equations 1 and 2. It also decreases the alkaline reserve of the concrete, leading to lower pH.

$$3\,CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}10H_2O_{(s)} + 2\,Cl^-_{(ac)} \rightarrow 3\,CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O_{(s)} + SO_4^{2-}{}_{(ac)} \quad (1)$$

$$3\,CaO{\cdot}Al_2O_{3(s)} + CaCO_{3(ac)} + 10\,H_2O_{(l)} \rightarrow 3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}10H_2O_{(s)} \quad (2)$$

Tricalcium aluminate reacts in the presence of sulfate ions forming ettringite or calcium sulfoaluminate which in the presence of chloride ions form calcium chloroaluminate (equ. 1), thus decreasing the risk of deterioration of the metal frames, with a limit of 8.6% C_3A [32], which establishes the maximum capacity of the concrete for combining chloride ions. Calcium carbonate also decreases the porosity of the concrete, thus decreasing the permeability of the entry of aggressive ions. However, Becker [34] recommends using cements with calcium carbonate content less than 10% for concrete exposed to marine environments, and in this study the pozzolanic cement contains 17.4% $CaCO_3$. Although cements that contain a calcium filler such as calcium carbonate are currently used due the low level of impact they have on the environment as a result of lower CO_2 emissions, studies by Kenai have shown that it is important to consider that cracking in concrete with this type of cement can be critical, especially in marine environments [36].

The physical, chemical and mechanical characteristics of the types of concrete used in this study are shown in Table 3. It can be seen the concrete types show slightly different initial pH, which is to be expected based on their oxide content and their pozzolan or calcium carbonate content, which leads to a fall in pH caused by the decreased alkaline reserve. Differences can be seen in characteristics such as total absorption and porosity, coefficient of capillary absorption (k), capillary sorption (m) and real porosity (ε_e), which is in agreement with the C_3A content of the Ordinary Portland cement, as this affects its initially higher compressive strength, because it has higher hydration temperature and speed, and it therefore hardens more rapidly. This means that at the early stage, the concrete prepared with Ordinary Portland cement has higher compressive strength, while that of the Pozzolanic concrete reaches the same strength over time and later surpasses it. As a result, porosity and absorption are higher in the Ordinary Portland concrete after 90 days of curing.

Table 3. Physical and mechanical properties of the two types of concrete.

Physical and mechanical variables	Concrete with Ordinary Portland Cement	Concrete with Pozzolanic Cement
pH	13.22	12.60
Initial concentration of free chloride ions (% Cl^- / cement)	5.67×10^{-2}	5.12×10^{-2}
Compressive strength at 28 days (MPa)	47.1	35.2
Compressive strength at 90 days (MPa)	51.2	52.3
Coefficient of capillary absorption, *k* (Kg m^{-2} $s^{-1/2}$)	9.92×10^{-3}	5.84×10^{-3}
Capillary sorption, *s* (m $s^{-1/2}$)	1.03×10^{-4}	9.03×10^{-5}
Real porosity, ε_e (%)	9.62×10^{-2}	6.30×10^{-2}
Total absorption (%)	2.3	1.69
Total porosity (%)	13.2	10.89
Resistivity (KΩ·cm)	48.2	50.6

Fig. 1 shows micrographs of the two types of concrete. It can be seen that the Ordinary Portland concrete has larger pores and microfissures can also be seen on its surface, while the Pozzolanic concrete shows smaller pores and a rougher more homogenous surface.

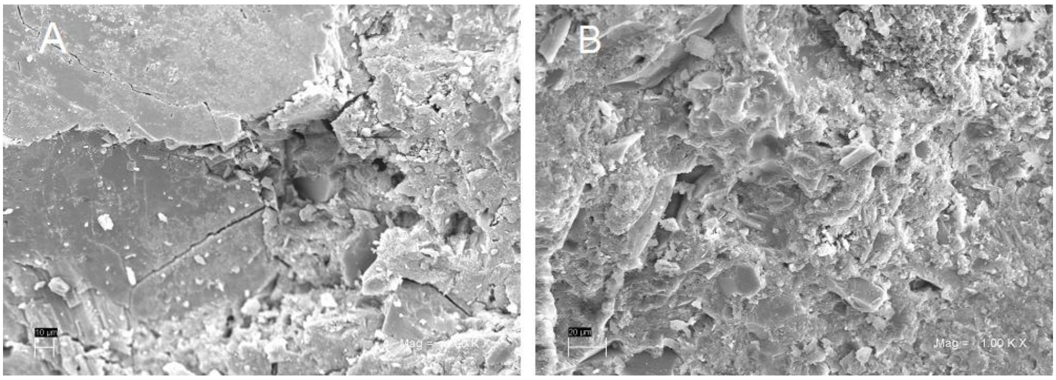

Figure 1. Micrographs of the two types of concrete obtained using a SEM. A) Ordinary Portland Concrete; B) Pozzolanic Concrete. (1000x) [26].

3.2. Corrosion Analyze

The variation over time of the average of three measurements of corrosion potential for the galvanized steel embedded in Ordinary Portland and Pozzolanic concrete are shown in Figure 2. The galvanized steel embedded in Ordinary Portland concrete shows initial values of corrosion potential around -650 mV_{sce}, while the bar embedded in Pozzolanic concrete gives values around 100 mVsce more negative, denoting a higher level of activity mainly due to the difference in pH between the concrete types. It is known that galvanized steel possesses a pH stability range of 6 to 12.5, within which the corrosion rate of the zinc is around 10 mpy or less [1]. This pH range increases to 13.3 [1, 7, 21, 25, 27] with the formation of calcium hydroxy-zincate (CHZ) as a corrosion product [29], which reaches is highest point of stability at this pH, presenting a more homogenous and compacted distribution over the zinc.

After the 50 cycles, the values of corrosion potential for the galvanized steel in the two types of concrete end at around -900 mV, indicating that the steel frame is still in a passive state. However, the variation in the values over time shows a better behavioral tendency for the galvanized steel embedded in the Ordinary Portland concrete due to the C_3A content in the pure Portland cement which, as explained above, reacts with the chloride ions, decreasing the level of activity of the metal's corrosion process.

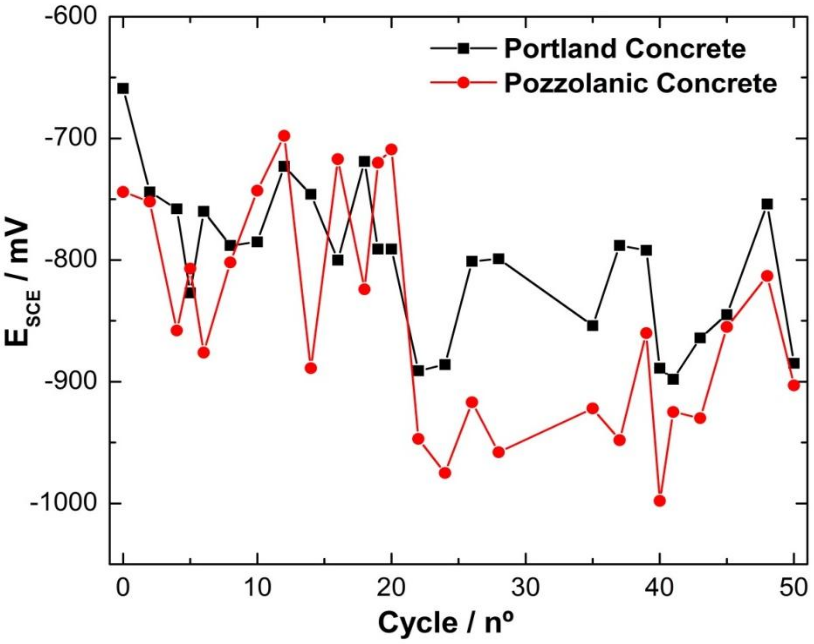

Figure 2. Variation over time of Corrosion Potential of the galvanized steel for the two concrete types.

Figure 3 shows the variation in the average corrosion current of the galvanized steel for the two types of concrete. Similar behavioral trends can be seen, though the current measured on the galvanized steel in the Portland concrete is slightly lower. Nevertheless, in both cases the galvanized steel bars remain in a passive state, which is in agreement with the values obtained for corrosion potential.

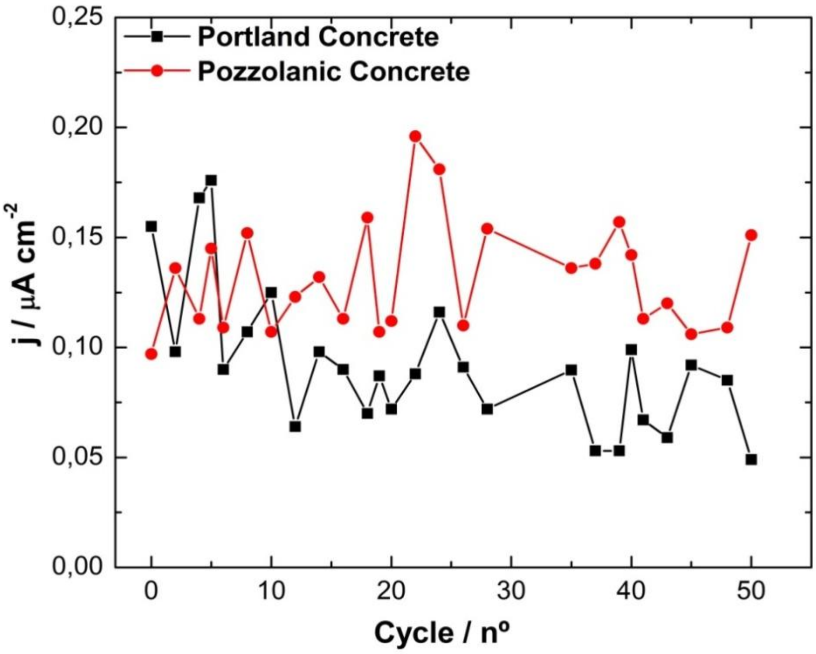

Figure 3. Variation over time in Corrosion Current of the galvanized steel in the two concrete types.

3.3. Quantification of free chloride ions and pH

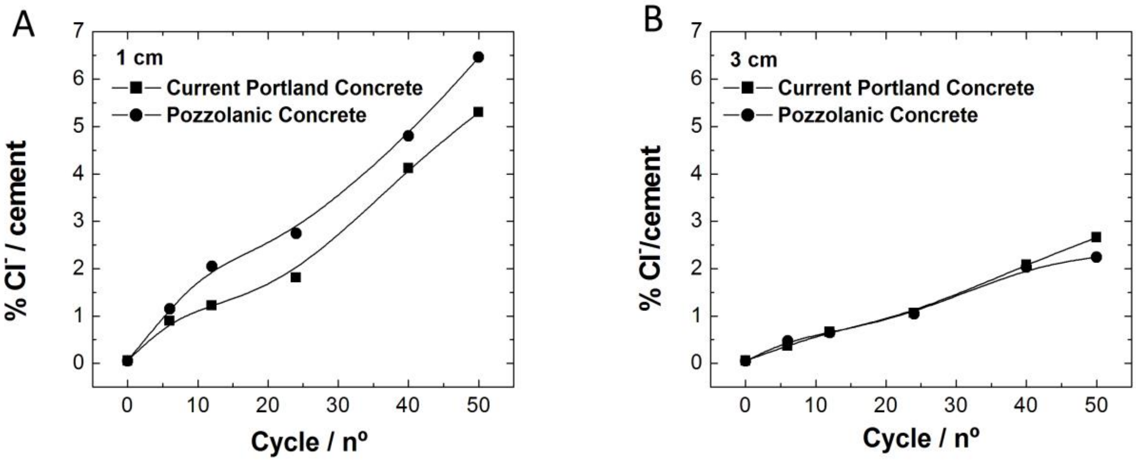

Figure 4. Comparison of free chloride ion concentration in the two concrete types. (A) 1 cm and (B) 3 cm.

The measurements of chloride ion concentration taken at different cycles and different depths (Figure 4A) show that there is higher chloride ion concentration in the Pozzolanic concrete at a depth of 1 cm (the depth furthest from the steel rebar), while at 3 cm (Figure 4B) where the galvanized steel bar is located, the free chloride ion concentration is similar for the two concrete types. The chloride ion diffusion coefficient (D_o) in the Pozzolanic concrete is 1.1×10^{-7} m^2 s^{-1} and in the Standard Portland concrete it is 2.0×10^{-8} m^2 s^{-1}. Therefore, the chlorides diffuse more rapidly in the Pozzolanic concrete even though it has lower porosity, as the Portland concrete contains C_3A which retains chlorides, as shown by the measurements of combined chloride content at a depth of 1 cm in the Portland concrete (1.10%) and in the Pozzolanic concrete (0.80%) and at 3 cm: 1.16% and 0.83%, respectively.

Figure 5 shows the different pH measurements obtained at different cycles on the zinc-concrete interface, for the two concrete types. The Ordinary Portland concrete maintains pH within the range of best stability for zinc corrosion products, between 13.3 and 12.5, while for the Pozzolanic concrete, pH varies between 12.5 and 11.2, a range in which the zinc is stable but the zinc corrosion products, such as calcium hydroxy-zincate [1, 7, 21, 25, 27] and simonkoleite [36] present decreased protective capacity, as they are more porous and more permeable to the entry of aggressive ions like the chloride ion.

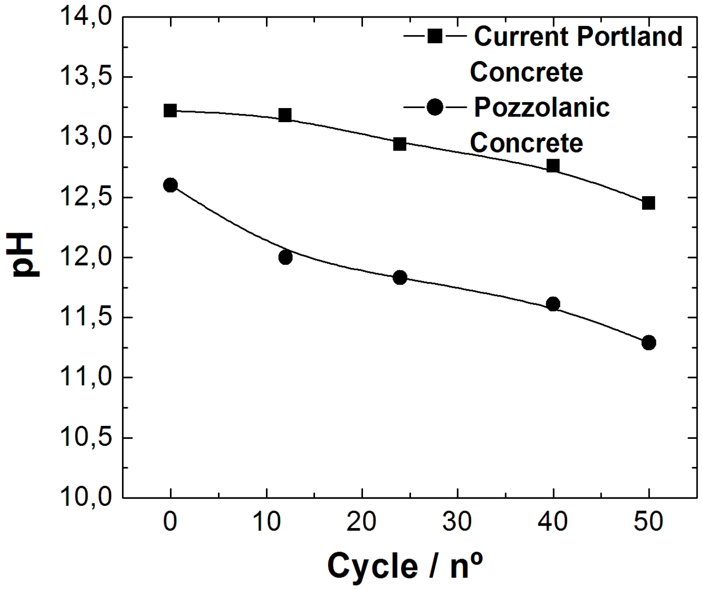

Figure 5. pH at a depth of 3 cm at cycles 0, 12, 24, 40 and 50.

3.4. Morphology and composition of the galvanized steel

The galvanized steel bars initially have a zinc coating with a thickness of approximately 80 µm, and after removing the specimens from the wet chamber the formation of a fine layer of corrosion products mainly composed of calcium hydroxy-zincate ($Ca(Zn(OH)_3)_2$ x H_2O) and zinc oxide (ZnO, zincite) was observed (Figure 6). The corrosion products formed on the galvanized steel embedded in the Ordinary Portland concrete were distributed homogenously over the Zn layer (Figure 7), while for the rebar embedded in the Pozzolanic concrete, the layer of corrosion product shows irregular thickness along its length (Figure 7B). These observations are in line with the data obtained for the chloride diffusion coefficients, which suggest that the chloride entry rate is not the same for both concrete types, though the final chloride content levels on the interface are similar.

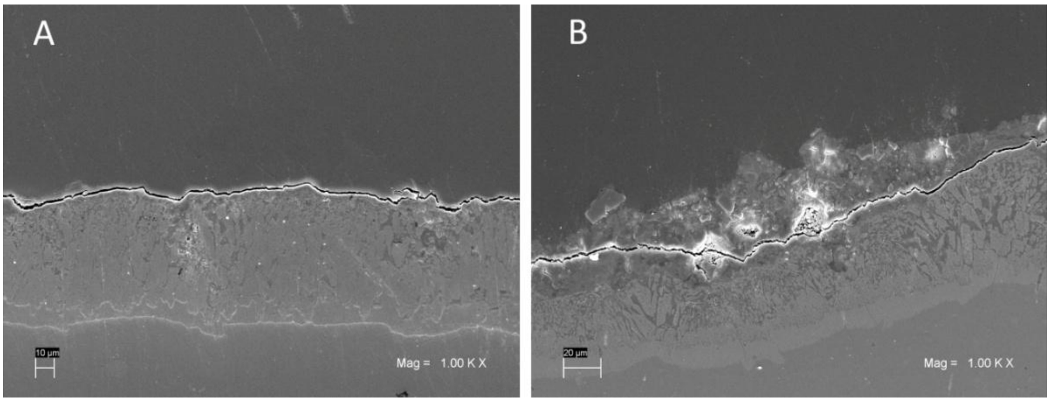

Figure 6. Cross-section micrographs of the galvanized steel obtained by SEM (A) before being embedded in the concrete (B) after removing the reinforced concrete from the wet chamber (1000x) [26].

The EDAX analysis of the corrosion products mainly shows the presence of chlorine in the corrosion products in the pozzolanic concrete, while the Portland concrete mainly shows the presence of calcium, zinc and oxygen, corroborating the presence of zincite (ZnO).

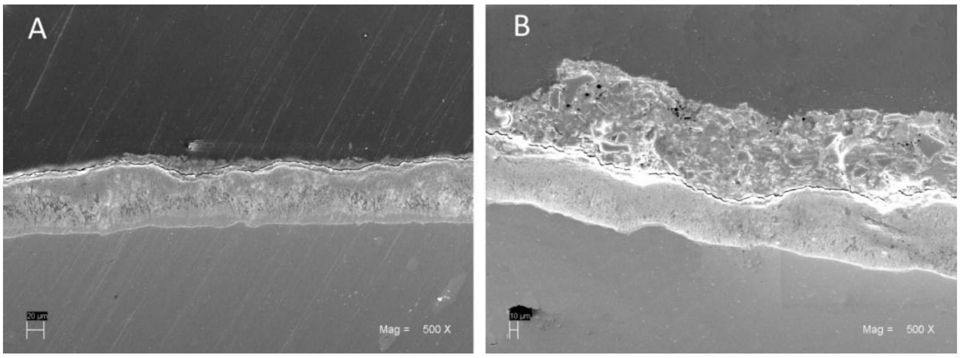

Figure 7. Cross-section micrographs of the galvanized steel bars after 50 cycles embedded in (A) Ordinary Portland concrete, and (B) Pozzolanic concrete. (500x)

3.5. Polarization Curves

Another method of evaluating the behavior of galvanized steel in the different concretes is to prepare anodic polarization curves in the presence of oxygen for the galvanized rebars in solutions from powdered pieces obtained from the concretes at different cycles of semi-immersion and drying (Fig. 8).

The anodic curve of the galvanized sample for the two solutions prepared from powder from the concretes before emersion in the solution containing chloride ions shows an area of anodic dissolution, with a maximum current of approximately 2.0 x 10^{-5} A cm^{-2} and a potential of around -690 mVsce, an area of passivity and an area of picking with a picking potential of around 900 mVsce. However, at cycle 12 of the experiment the curve of the galvanized steel in the Portland concrete solution (Pp) maintains its shape but shifts to higher currents in one period and decreases its corrosion potential by around 60 mVsce, unlike the behavior in the Pozzolanic concrete solutions (Pz), where the current increases to 4.0 x 10^{-3} A cm^{-2} and the potential decreases to -980 mVsce due to the presence of chloride. At cycle 50, due to the higher chloride content, the galvanized steel presents less passive behavior for both concrete types, reaching higher current by around 10^{-2} A cm^{-2}. The behavior of the galvanized steel in both situations also corresponds to the difference in pH of the concrete types and the stability of the corrosion products formed under these conditions. The results of polarization curves corroborate those obtained in the other experiments of this study, like corrosion potential, corrosion current and morphology of the galvanized steel.

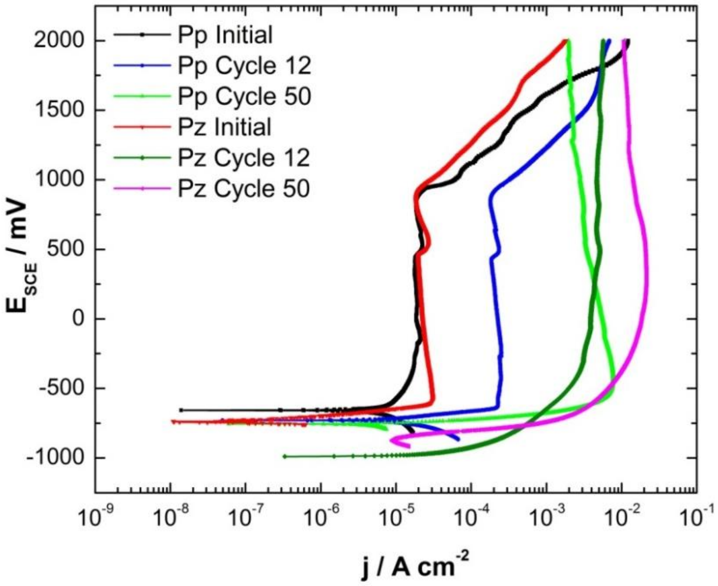

Figure 8. Polarization curves for galvanized steel rebars embedded in (A) Standard Portland concrete and (B) Pozzolanic concrete

4. CONCLUSIONS

The results obtained in this study from concrete reinforced specimens with galvanized steel rebars, using accelerated chloride ion exposure assays, electrochemical testing, characterization of the rebars and the concrete prepared with two types of cement, lead to the following conclusions:

The galvanized steel bar embedded in the concrete with a higher calcium filler content (calcium carbonate) shows inferior behavior than the bar in pure Portland concrete in terms of the formation of corrosion products in an atmosphere of chloride ions.

The quality of the cement must be studied in terms of C_3A content and calcium filler content before being used, as these factors influence the feasibility of chloride ion penetration, and therefore affect the durability of reinforced concrete structures.

The corrosion products on the galvanized steel obtained from the concrete sample prepared with Portland cement are mainly comprised of Zincite (ZnO), while the concrete prepared with

Pozzolanic cement also shows the presence of calcium hydroxy-zincate, $Ca(Zn(OH)_3)_2 \cdot H_2O$ and, to a lesser degree, the formation of simonkoleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$).

The non-homogenous distribution of corrosion products formed on the galvanized steel in samples of concrete prepared with Pozzolanic cement corroborates the conclusion that access of chloride ions to the rebar is heterogeneous, possibly due to undetected C_3A content in this concrete.

At the end of the experiment, at cycle 50, with an average chloride concentration on the rebar-concrete interface of 2.5% chloride/cement, the galvanized steel bars still remain in a passive state in both concrete types.

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References

1. SR. Yeomans, Galvanized Steel Reinforcement in Concrete: An Overview, Elsevier, 2004.
2. O. Troconis de Rincón and DURAR Network Members, Manual for Inspecting, Evaluating and Diagnosing Corrosion in Reinforced Concrete Structures, CYTED, ISBN 980-296-541-3, Maracaibo, Venezuela (2000).
3. Bilal S. Hamad, John A. Mike, *Constr.Buil. Mater.* 19 (2005) 275.
4. R. Vera, M. Villarroel, A.M. Carvajal, E. Vera, C. Ortiz, *Mater. Chem. Phys.* 114 (2009) 467.
5. Véronique Bouteiller, Christian Cremona, Véronique Baroghel-Bouny, Aurélie Maloula, *Cement Concr. Res.* 42 (2012) 1456.
6. P. Dangla, W. Dridi, *Corros. Sci.* 51 (2009) 1747.
7. A. Bautista, J.A. Gonzalez, *Cement Concr. Res.* 26 (1996) 215.
8. P. Ghods, O. Burkan Isgor, F. Bensebaa, D. Kingston, *Corros. Sci.* 58 (2012) 159.
9. M.V.A. Florea, H.J.H. Brouwers, *Cement Concr. Res.* 42 (2012) 282.
10. Ueli M. Angst, Bernhard Elsener, Claus K. Larsen, Øystein Vennesland, *Corros. Sci.* 53 (2011) 1451.
11. Marco Manera, Øystein Vennesland, Luca Bertolini, *Corros. Sci.* 50 (2008) 554.
12. Y. Morozov, A.S. Castela, A.P.S. Dias, M.F. Montemor, *Cement Concr. Res.* 47 (2013) 1.
13. Ki Yong Ann, Ha-Won Song, *Corros. Sci.* 49 (2007) 4113.
14. E. Zornoza, J. Payá, P. Garcás, *Corros. Sci.* 50 (2008) 1567.
15. N. Gowripalan, H.M. Mohamed, *Cement Concr. Res.* 28 (1998) 1119.
16. B. Reddy, G.K. Glass, P.J. Lim, N.R. Buenfeld, *Cement & Concrete Composites* 24 (2002) 1.
17. Yuxi Zhao, Jiang Yu, Weiliang Jin, *Corros. Sci.* 53 (2011) 3388.
18. J.J. Assaad, C.A. Issa, *Constr. Build. Mater.* 30 (2012) 667.
19. I. Fayala, L. Dhouibi, X.R. Nóvoa, M. Ben Ouezdou, *Cement & Concrete Composites* 35 (2013) 181.
20. P. Pedeferri, *Constr. Build. Mater*. 10 (1996) 391.
21. T. Bellezze, M. Malavolta, A. Quaranta, N. Ruffini, G. Roventi, *Cement & Concrete Composites* 28 (2006) 246.
22. E. Sistonen, A. Cwirzen, J. Puttonen, *Corros. Sci.* 50 (2008) 3416.
23. S. Yeomans, Corrosion of the zinc alloy coating in galvanized reinforced concrete, Corrosion 98, paper nº 653.
24. S.B. Farina, G.S. Duffó, *Electrochim. Acta* 52 (2007) 5131.

25. Z.Q. Tan, C.M. Hansson, *Corros. Sci.* 50 (2008) 2512.
26. J. Román, R. Vera. M. Puentes, M. Bagnara, A.M. Carvajal, P. Rojas, *Revista de la Construcción* 12 (2013) 30.
27. Shuan Liu, Huyuan Sun, Lijuan Sun, Huiji Fan, *Corros. Sci.* 65 (2012) 520.
28. F.J. Recio, M.C. Alonso, L. Gaillet, M. Sánchez, *Corros. Sci.* 53 (2011) 2853.
29. F. Tittarelli, T. Bellezze, *Corros. Sci.* 52 (2010) 978.
30. Rita Ghosh, D.D.N. Singh, Kinetics, *Surf. Coat. Technol.* 201 (2007) 7346.
31. A. Macias, C. Andrade, *Corros. Sci.*, 30 (1990) 393.
32. J.C. Orellan Herrera, G. Escadeillas, G. Arliguie, *Cement and Concrete Research* 36 (2006) 1939.
33. V. L. Bonavetti, V. F. Rahhal, *Revista de la Construcción*, 5 (2006) 33.
34. E. Becker. Cemento Portland con Filler Calcáreo. Propiedades y recomendaciones de uso. Loma Negra (2000).
35. Madani Bederina, Zoubir Makhloufi, Tayeb Bouziani, *Physics Procedia* 21 (2011) 28.
36. J.D. Yoo, P. Volovitch, A. Abdel Aal, C. Allely, K. Ogle, *Corros. Sci.* 70 (2013) 1.