

Performance of Carbon Steel and Galvanized Steel in Reinforced Concrete Structures after Accelerated Carbonation

Rosa Vera^{1,*}, Ricardo Venegas¹, Ana María Carvajal², Francisco Corvo^{3,4}, Tezozomoc Pérez³

¹Instituto de Química, Facultad de Ciencias, Pontificia Universidad Católica de Valparaíso, Avda. Universidad 330, Placilla, Valparaíso, Chile,

²Escuela de Construcción Civil, Facultad de Ingeniería, Pontificia Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Macul, Santiago, Chile

³Centro de Investigación en Corrosión (CICORR), Universidad Autónoma de Campeche, Ave. Agustín Melgar s/n, Col. Buenavista, San Francisco de Campeche, C.P.24030, México e Instituto de Ciencia y Tecnología (IMRE), calle Zapata esq. a G, Vedado, Plaza, Habana, Cuba.

⁴Instituto de Ciencia y Tecnología (IMRE), calle Zapata esq. a G, Vedado, Plaza, Habana, Cuba.

*E-mail: rvera@ucv.cl

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The aim of this paper is to study the effects of carbonation on the electrochemical properties of carbon steel and galvanized steel, immersed into cubic prisms of concrete elaborated with Portland pozzolanic cement. Reinforced concrete specimens using these two metallic materials were exposed in a carbonation chamber. In a short time period changes in carbon steel and galvanized steel potentials and in concrete resistivity indicated an increase in carbonation of steel rebar. During the test period it was observed that zinc, instead to be in active conditions, attains lower corrosion rate than carbon steel. This behavior allows to assume the use of galvanized steel as an option to enlarge useful life of reinforced concrete structures in carbonated environments.

Keywords: corrosion, carbonation, concrete, galvanized steel, carbon steel

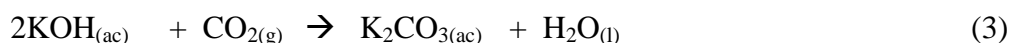
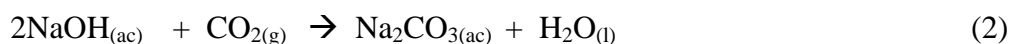
1. INTRODUCTION

In the recent decades several research work have been performed concerning the durability of reinforced concrete structures used in highly aggressive environments such as marine or industrial areas in which ordinary steel rebars show high levels of deterioration due to electrochemical corrosion [1-4].

In marine environments ordinary steel suffers pitting corrosion due to the presence of chloride ions from airborne salinity. These ions diffuse through pores in the concrete, and become inserted in

the crystalline network of the oxide layer responsible for the passivation of the steel, thus initiating a process of autocatalytic oxidation [5-8].

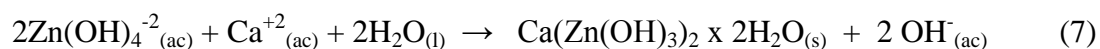
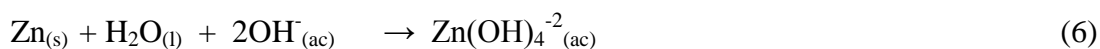
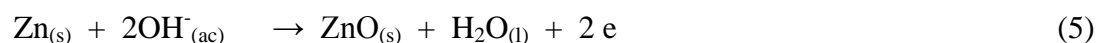
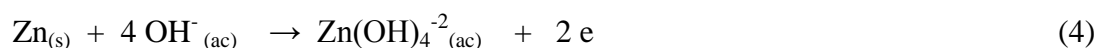
Furthermore, in industrial or urban areas where CO₂ emissions have considerably increased over time, carbonation in concrete structures has also risen. As it is well known, when this gas diffuses through the pores in the concrete it reacts with the alkaline ions dissolved in the pores of solution, initiating carbonation as described in equations 1, 2 and 3, and leading to a decrease in pH on the steel-concrete interface, reaching values lower than 9.5, and causing de-passivation of the steel structure [9-11].



One way to maintain the expected durability of the structure and diminish carbonation rate is the use of galvanized steel. Zinc is stable in the pH range of 6 to 12.5, even more than carbon steel, the stability of the last is observed for pH values between 10 and 12.5. Under these conditions, the corrosion products formed on the surface of the galvanized steel, mainly CaHZn (calcium hydroxy-zincate, Ca(Zn(OH)₃)₂ x 2H₂O), are more compact, homogenous, adherent and less voluminous than the oxides formed on carbon steel [12-17].

Sosa-Baz et al. report the presence of simonkolleite (Zn₅(OH)₈Cl₂.H₂O), zincite (ZnO), wulfingite (Zn(OH)₂), calcite (CaCO₃), portlandite (Ca(OH)₂) and calcium and aluminum oxides (Ca₅Al₆O₁₄ and Ca₁₂Al₁₂O₁₉) on the zinc-concrete interface from a film of thermal zinc spray in a system of cathodic protection via galvanic anode. It is argued that the compounds formed are greater in volume and therefore block the pores, increasing resistivity and reducing the efficiency of cathodic protection. Similarly, the pores on the galvanized steel-concrete interface can be obstructed with products of zinc corrosion, thus decreasing the rate of corrosion of the embedded rebar [18-19].

The sequence of reactions that best represents the Zn corrosion process in alkaline media is the following [20]:



However, a disadvantage to the use of galvanized steel is that the corrosion rate increases greatly in media with pH above 12.5, enabling the evolution of hydrogen, the main consequence of

which would be the formation of hollows over the rebar-concrete interface, reducing the area of contact between the galvanized steel and the hydrated phases of the cement, with possible loss of metal-steel adhesion [21].

This highlights the importance of studying the behavior of galvanized steel in concretes made using pure Portland cement mixed with pozzolana, produced in Chile, as the reaction of the different cements with water generates a pH that depends on the alkaline content of the given cement amount of sodium and potassium ions.

The present paper analyses the effects of carbonation on the electrochemical properties of carbon steel and galvanized steel in the concrete mix as a consequence of exposure of reinforced concrete specimens in an accelerated carbonation chamber.

2. MATERIALS AND METHODS

2.1. Design of test-probe

Cubic specimens, 15 cm along each edge, were fabricated of reinforced concrete using Portland Pozzolanic cement of standard quality. Cement composition is shown in Table 1. Concrete samples were elaborated with a water/cement ratio (w/c) of 0.55, dosage was in accordance with the amounts shown on Table 2. The design of the reinforced concrete test-probe used in the study contains a total of 2 carbon steel and 2 galvanized steel rebars located 3.5 cm from the perimeter of the cube; the bars have a diameter of 3/8" and a length of 16 cm.

Table 1. Cement composition (%)

Compound	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	Mn ₂ O ₃	P ₂ O ₅
Content, %	21.5	4.6	3.3	62.0	2.7	0.2	0.4	2.2	0.08	0.09

Compound	TiO ₂	P.I	Free CaO	C ₃ S	C ₂ S	C ₄ AF	C ₃ A	Sup. m ² Kg ⁻¹	Esp.	Pozzolana, maximum content of total cement
Content, %	0.30	2.8	0.5	66.0	16.0	11.14	6.6	360		29.7

Table 2. Content by m³ of concrete

Mixture	Portland Pozzolana Cement (Kg)	Water (L)	Gravel (Kg)	Sand (Kg)
w/c: 0.55	308	171	1039	959

The galvanized steel probes comply with ASTM Standard A767M and are identified with the letter G, and the carbon steel of type A44-28H of commercial use is identified with the letter C.

The probes were cured in a wet chamber at 25 °C and 90% relative humidity for 28 days. Cubic concrete probes were also fabricated without steel rebars in order to characterize the concrete mix. Both, fine and coarse aggregates used were siliceous.

2.2. Concrete mix characterization

The concrete mix was characterized by testing compressive strength and electrical resistivity using probes without steel rebars. Compressive strength (ASTM Standard C39) was evaluated from day 28th of curing in the wet chamber until day 60th. Cylindrical core samples were also taken from some non-reinforced specimens after the curing period in order to measure the electrical resistivity of the concrete. Measurements were taken in accordance with the method of Wenner [9].

2.3. Accelerated carbonation chamber test

General conditions in the carbonation chamber were: relative humidity of 60-70% and temperature of 25 °C. The purpose of the testing is to cause accelerated diffusion of carbon dioxide through the pores in the concrete towards the rebars, in order to evaluate the resistance of both types of steel to carbonation, which leads to corrosion of the steel rebars, and to see how the different degrees of carbonation affect resistivity of the concrete. The probes were partially removed at 28, 35, 42 and 49 days of exposure in carbonation chamber, which is maintained saturated with CO₂ (100% CO₂). All faces of the cubic specimens, except the bottom one, which supports the probe inside the chamber, were exposed to gas penetration.

2.4. Electrical Resistivity for each time

Electrical resistivity measurements using the Wenner method were taken throughout the progress of carbonation of the probes, that is, for each partial removal of the concrete samples, a core sample was extracted having the same carbonation time as the probe. Thus, by the end of the accelerated carbonation test, changes in electrical resistivity of concrete were obtained as function of carbonation time.

2.5. Electrochemical measurements

Each time the reinforced concrete samples were partially removed from the carbonation chamber, the status of the embedded rebars was evaluated by measuring corrosion potential and corrosion current. This was done using a G-Sec potentiostat V2.0, forming an electrochemical cell with a Cu/CuSO₄ reference electrode (CSE +316mV v/s ENH), a copper counter-electrode, and with the steel rebar as the working electrode.

Measurement of corrosion potential (E_{corr}) were done for 30 minutes until a stable potential was reached. Polarization resistance (R_p) was then measured by making a sweep of potential of ± 10 mV over the E_{corr} found for the rebars. This value was then used to indirectly calculate the corrosion current and with that the corrosion rate of the rebar by Stern and Geary equation (ec. 8). [22]

$$I_{\text{corr}} = \frac{B}{R_p} \quad (8)$$

Where R_p is the polarization resistance, and B is a constant value determined from Tafel plot through non destructive experiments in concrete probes [23], B has two values, 26 mV to active carbon steel and 56 mV to passive rebars. In the case of galvanized steel this constant value was taken from Farina studies, it is 26 mV [24]. To convert the corrosion current into corrosion rate, it applies Faraday's law. The results obtained were compared with measurements taken on a non exposed probe, denominated the control probe or "C probe".

2.6. Qualitative and quantitative analysis of the carbonation level of the specimens

Qualitative analysis was performed by cutting each specimen in two equal parts and exposing its interior. The two resulting interior faces were then sprayed with a phenolphthalein solution: an acid-base indicator that in alkaline solution, such as with healthy concrete, turns violet in color, while in neutral or acidic solution it remains colorless. This method can be used to measure the depth reached by the entrance of CO_2 into the probe. The consequence of the diffusion of the gas is a fall in pH in the concrete and therefore there will be no coloration when spraying with phenolphthalein.

Subsequently, quantitative analysis was performed by taking samples of crushed concrete from each probe at different depths: 1, 2, 3 and 4 cm from the surface of the probe up to the rebars. These samples were then submitted to a soluble salt extraction process using deionized water to collect the ions responsible for the pH in the concrete pore solution. The pH of the resulting solution was measured with a Corning Scholar 425 pH meter with a glass membrane electrode calibrated between pH 7 and 10, with a gradient of 92%, obtaining carbonation profiles as function of sample depth.

3. RESULTS AND DISCUSSION

3.1. Characterization of the concrete

Figure 1 shows the average variation in compressive strength of the concrete probe over time. Compressive strength for the cubes used in these tests increases from 25.3 MPa at 28 days wet chamber curing to a maximum of 30.8 MPa at 49 days curing. This value is concordant with the literature [9], due it falls between the compressive strength of a cubes with a w/c ratio of 0.45 and with a ratio of 0.65.

Figure 2 shows the average variation in electrical resistivity versus time, for samples with and without carbonation. A trend to decrease resistivity in the first days of exposure can be seen due to humectation of the specimens when they are initially placed in the wet chamber, after the initial behavior, resistivity begins to increase due to the formation of calcium carbonate which, as it is deposited in the pore, cuts conductivity between the ions occluded in the pore. The calcium carbonate occupies a larger volume in the pores of the concrete than the calcium hydroxide without carbonation. It could cause less connectivity between the pores which would help to increase surface impermeability, and therefore less conductivity inside the concrete, which substantiates the resistivity values found.

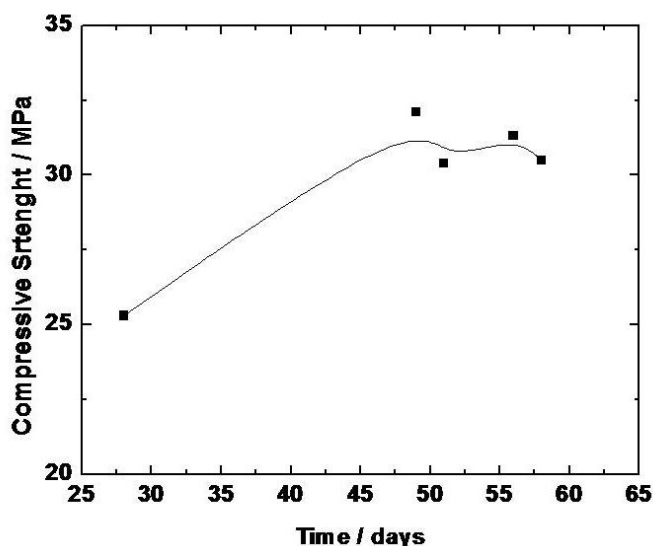


Figure 1. Compression resistance over time.

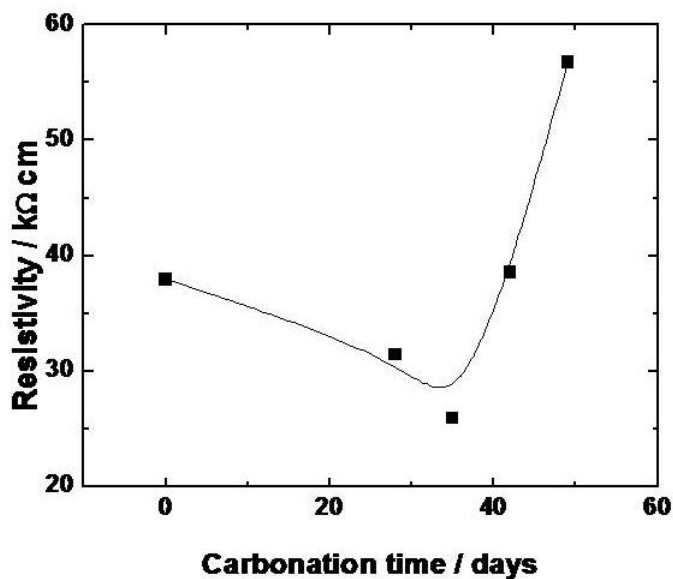


Figure 2. Electrical resistivity of the samples.

3.2. Carbonation Process

The photographs in Figure 3 show cross-sections of the concrete specimens exposed in the accelerated carbonation chamber. It can be seen how the degree of carbonation varies depending on the number of days of exposure in the carbonated environment.

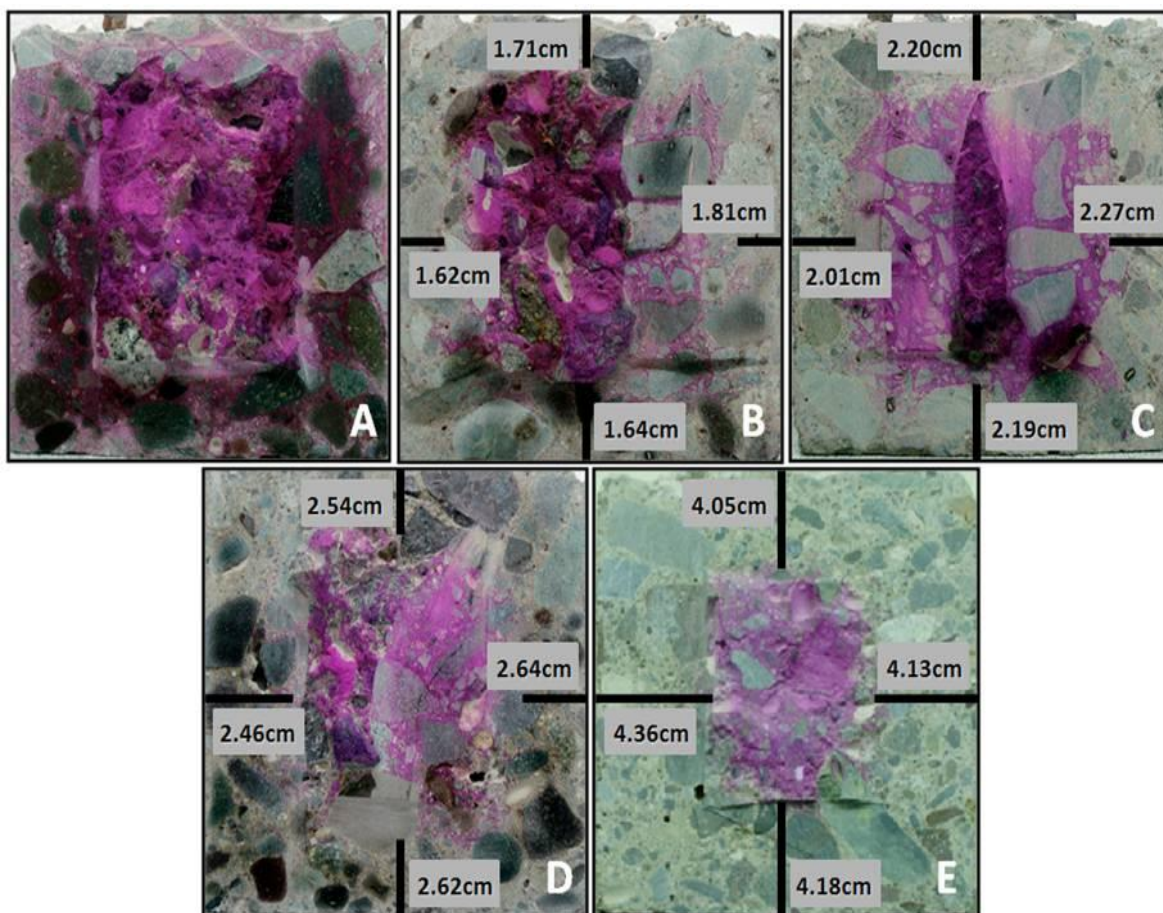


Figure 3. Concrete probes exposed in the carbonation chamber A) 0 days, B) 28 days, C) 35 days, D) 42 days, E) 49 days.

The penetration of CO₂ over time into the samples was confirmed by wet chemistry using phenolphthalein, and it can be seen in the change in coloration on the surface of the concrete, where the areas without carbonation are violet in color, corresponding to the interaction between the phenolphthalein indicator and the ions responsible for the alkaline pH of the concrete. The areas without color change show the advancement of the gas into concrete and its capacity to combine with the water in solution in the pores and to react with dissolved alkali, leading to a subsequent drop in alkalinity due to the neutralization of the pH level [9-11].

The initial state of the probe after 28 days of curing in the wet chamber (Figure 3A) shows healthy concrete with an alkaline pH, free of contamination. After 28 days of exposure in the accelerated carbonation chamber, the development of carbonation has reached an average penetration

depth of 1.7 cm (Figure 3B), and thus has not yet reached the rebar. At 35 days exposure, diffusion of CO₂ can be seen to an average depth of 2.2 cm; at 42 days it has reached 2.6 cm and at 49 days, 4.18 cm. The average carbonation depths determined by wet chemistry are expressed as a function of time (Figure 4).

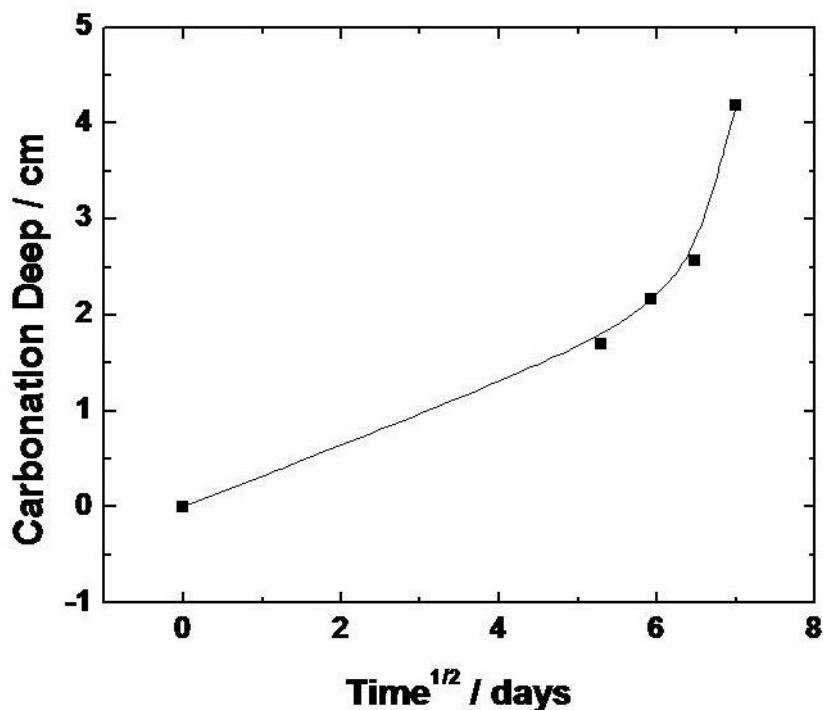


Figure 4. Carbonation depths as a function of exposure time in the accelerated carbonation chamber.

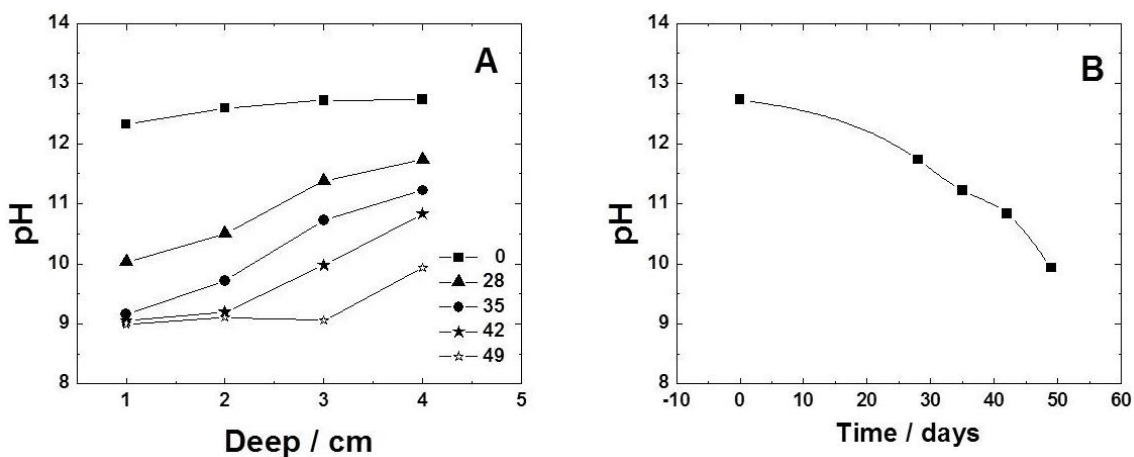


Figure 5. A) pH profile for different CO₂ exposure times. B) pH at the steel/concrete interface as a function of time.

The most common method for predicting the CO₂ penetration depth reached in a reinforced concrete structure at a particular time relates the depth with the root squared of the time in years. However, in this case, the process is accelerated and obeys a system that does not follow that pattern as we are working in a saturated CO₂ environment. This irregular development is also due to the

heterogeneity of the concrete paste. Although it is made using the correct amounts and mixed in accordance with normal construction standards, non-homogenous zones are formed, in which these properties are shown [22-23].

In order to quantify the degree of carbonation, profiles were obtained by measuring the pH of solutions obtained by leeching soluble salts from crushed concrete. As can be seen in Figure 5, before exposure the pH of the normal concrete is around 12.6 from the perimeter to the area around the rebar, while after 28 days of exposure, at 1 and 2 cm from the perimeter the pH falls 2 units, in agreement with the observations carried out on the cross-section of the same specimen, where it was found that the carbonation depth was around 1.7 cm. At 3 and 4 cm there are also drops in the initial pH value of 12.7 to 11.7, this is because the CO₂ diffuses faster through larger pores; however, the fall in pH is not generalized to all points of the surface because the concentration of the gas at these points is still insufficient to cause total carbonation at the given depth.

At 35 days it can be seen that the pH continues to drop, the first point has reached pH 9 and the deepest point, around the rebar, remains at 11; at 42 and 49 days exposure, the pH of the first two points (or of the perimeter of the probe) reached a value of 9, while inside the specimen, the pH reached approximately 9.9 because the carbonation rate is slower due to the fact that carbon dioxide takes longer to diffuse to the rebar due to the thickness of the concrete and a layer rich in Ca(OH)₂ around the bar.

3.3. Electrochemical testing

3.3.1. Corrosion Potential

The corrosion potentials of the carbon steel and the galvanized steel shown in Table 3 are the averages of the measurements taken at different exposure times in the accelerated carbonation chamber. The measurements at the start of the experiment for the steel in the C specimen, the control that was not submitted to carbonation, were -45.5 mV vs (Cu/CuSO₄) for carbon steel indicating low probability of corrosion [9-24] and -425 mV for galvanized steel vs (Cu/CuSO₄). These values will be used as reference for comparing the change in potential during the experiment.

Table 3. Corrosion potential for carbon steel and galvanized steel, carbonation depth and pH in the area around the rebars as a function of exposure time in the carbonation chamber.

Exposure time (days)	E _{corr} (Cu/CuSO ₄) (mV)		Carbonation depth (cm)	pH around the rebar
	Carbon steel	Galvanized steel		
0	-45.5	-425.0	0	12.6
28	-94.6	-504.5	1.7	11.7
35	-167.4	-629.2	2.2	11.2
42	-207.0	-754.3	2.6	10.8
49	-317.3	-976.5	4.2	9.9

The carbonation front reaches the rebar at some time between 42 and 49 days. The progressive activation of the steel and galvanized rebars can be seen during the period studied. Ijes [25] mentions the evolution in corrosion potential as the carbonation depth closes in on the concrete-steel interface. Monitoring the potentials allows confirmation of this trend, as the E_{corr} decreases even before the carbonation reaches the metals. The pH of the concrete at 49 days shows it is in the region of zinc oxide stability, in accordance with the Pourbaix diagram [26]; this reduces the corrosion rate even when the corrosion potential is more negative and is located in the active region.

The change in corrosion potential as a function of exposure time is more notable for galvanized steel, for which at 49 days the potential decreases by 551.5 mV vs (Cu/CuSO₄), while for the normal steel it only decreases by 271.8 mV vs (Cu/CuSO₄), in comparison to the initial value. Similar results were obtained by Moreno et al. [19].

3.3.2. Rate of corrosion

Though it is true that potentials are an indication of the probability of corrosion, the dominant factor to corroborate the active or passive state of a metal or alloy is corrosion current (I_c). Figure 6 shows two completely opposite trends, while the current density of the carbon steel increases almost linearly with exposure time in the accelerated carbonation chamber, the current determined for galvanized steel increases up to 35 days of exposure, the increment then becomes slight and remains constant after 49 days of exposure.

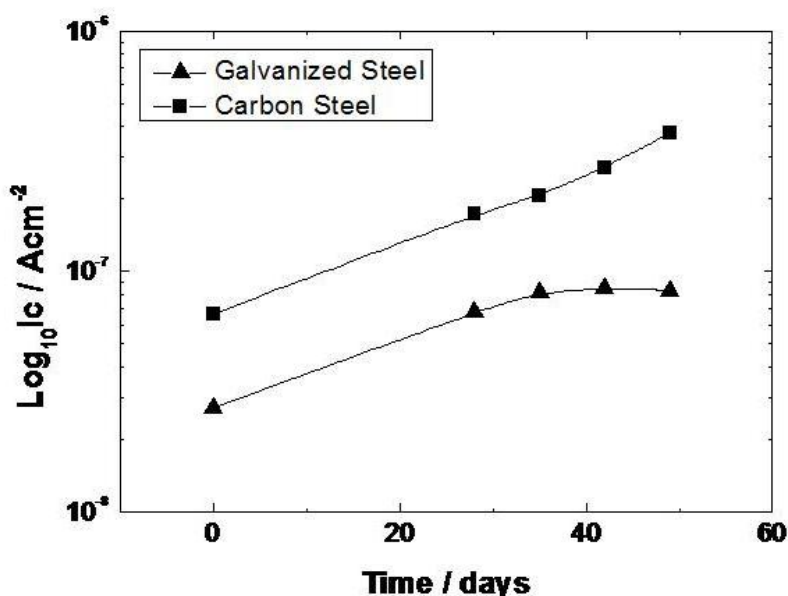
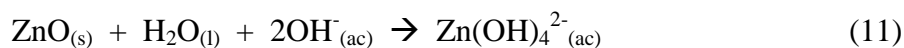
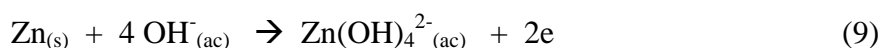


Figure 6. Variation in corrosion current for carbon steel and galvanized steel as a function of exposure time.

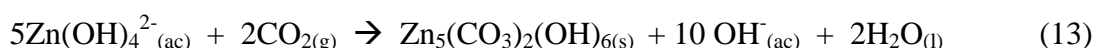
The behavior shown by the galvanized steel, as seen in Figure 6, suggests two stages with regard to the formation of corrosion products:

a) Initial exposure:

When setting, the concrete has only the alkalinity given to it by the alkaline metal oxides and alkaline earth metal oxides, where calcium plays a fundamental role as it stabilizes the hydroxy-zincate ions and makes them precipitate; the nucleation of this compound at pH lower than 13.3 (the pH of concrete is below this value) generates very fine and compact crystals that are then deposited and adhere to the surface of the galvanized steel, finally carrying the material to the passive state. Therefore, the corrosion product formed under these conditions is calcium hydroxy-zincate [HZC] ($\text{Ca}(\text{Zn}(\text{OH})_3)_2 \times 2\text{H}_2\text{O}$) (18), with the following reaction sequence:



b) Presence of carbonation: As the carbonation front advances into the concrete, it leads to a new corrosion product as the carbon dioxide becomes soluble and neutralizes the alkaline pH and forms carbonate and bicarbonate ions, causing the following reaction:



This stabilizes approximately at 35 days exposure. This compound shows different electrochemical behavior to that of the calcium hydroxy-zincate, which gives stability at a current of around $10^{-8} \text{ A cm}^{-2}$.

The corrosion rate obtained from the corrosion current found using the equation from Stern and Geary, for the carbon steel at the end of the test period, was a rate of $4.38 \mu\text{m y}^{-1}$ which is approximately 6 times the initial value ($0.77 \mu\text{m y}^{-1}$). Figure 7 shows the surface appearance of the carbon steel at the initiation of the experiment and after 49 days exposure in the carbonation chamber.

At the initiation of the experiment the corrosion rate of galvanized steel was $0.45 \mu\text{m y}^{-1}$; it increased to a lower rate respecting carbon steel up to 35 days and then remained constant until 49 days ($1.25 \mu\text{m y}^{-1}$). The increment in corrosion rate was approximately 3 times the initial rate by the end of exposure. The trend shows this variable did not change considerably with time, as the pH at this exposure time was 10.38 and at this rate would continue decreasing slightly to a value below 10, in a zone of oxide and hydroxide stability on the surface of the zinc [27].

Figure 8 shows the surface appearance of the galvanized steel at the initiation of the experiment and after 49 days of exposure in the carbonation chamber. The presence of corrosion products formed

with a certain degree of compactness can be observed, thus acting as a barrier to the corrosion of the bar. If the short-term trend continued, the corrosion rate of the galvanized steel rebar would be lower, and therefore the durability of a structure using this material would be longer respecting a structure using carbon steel in the same conditions of manufacture and exposure. This result is concordant with results reported by Andrade et al. [28].



Figure 7. Surface appearance of the carbon steel at the beginning of the experiment and after 49 days.



Figure 8. Surface appearance of the galvanized steel at the beginning of the experiment and after 49 days.

4. CONCLUSIONS

Galvanized and carbon steel bars are susceptible to corrosion by carbonation of concrete when they are used as reinforced. It is confirmed by changes toward more negative potential values during the test and incremented corrosion rates in both cases.

Under accelerated conditions in a carbonation chamber, corrosion rate is lower for galvanized steel. It tends to reduce at increasing exposure time, which would imply an increased durability of a concrete structure using this material rather than conventional carbon steel under conditions of advanced carbonation of the concrete.

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