

Efficiency of Galvanized Steel Embedded in Concrete Previously Contaminated with 2, 3 and 4% of NaCl

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The results are reported from the evaluation of corrosion rate of galvanized steel embedded in concrete specimens contaminated with different concentrations of NaCl and exposed to a simulated marine environment for a period of 320 days to compare their efficiency with steel-1018 used worldwide. The mixture was designed according to the standard ACI 211.1 considering a resistance of 250kg/cm² at 28 days. Was evaluated the potential corrosion (ASTM C 876-99 standard) and corrosion rate with the electrochemical technique of linear polarization resistance (LPR). The results show a significant protection against the corrosion of galvanized steel bars after 138 days of exposure when is embedded in an uncontaminated concrete. Was observed that in contaminated concretes the performance of galvanized as protection against corrosion is not efficient; is only a viable option to increase the service life of concrete structures with their respective limitations.

Keywords: Corrosion, Concrete, Galvanized, Sea Environment, Chlorides

1. INTRODUCTION

The steel in concrete structures is protected from the environmental aggression due to the highly alkaline environment (pH=12.5) that provides the pore solution. This environment forms a passive layer on the steel surface. The passive layer is destroyed as a result of the loss of alkalinity in the pore solution surrounding the steel and the entry of aggressive ions which chlorides are the most

aggressive. As described in the literature of this subject as extensive, the costs generated by the maintenance of the structures damaged by corrosion is only in the United States of thousands of millions of dollars quantified [1,2,3] but is present in almost all regions in the world where reinforced concrete structures (RCS) build up, and conditions exist to start the corrosion of steel. But is present in almost all regions of the world where build reinforced concrete structures and there are conditions that initiate the steel corrosion according to the national plan for evaluation of degradation by corrosion in bridges (SIPUMEX), there are in Mexico 6,500 bridges in federal road network which 7.5% required some type of repair and maintenance of corrosion problems [4]. One of the possible solutions to this problem is the use of galvanized steel, this is because the active metal coating on AISI steel-1018 such as zinc, not only provides simple barrier protection but also additional cathodic protection in which the coating act as an anode of protection in the event that the underlying steel is exposed [5,6,7,8,9] and in simulated concrete pore solution [10]. Exist researches which demonstrates the efficiency of the galvanized, however, the most of these works only study performed in clean concrete immersed in sea water but has not studied the specific effect of a previously contaminated concrete with NaCl (from its fabrication) in the process of corrosion or zinc protection in the steel bars.

The objective of this research was to evaluate the kinetics of corrosion of galvanized steel embedded in concrete specimens contaminated with different concentrations of NaCl and exposed in a sea environment and simulated for a period of 320 days, to compare their efficiency with the AISI 1018 steel used worldwide.

2. EXPERIMENTAL

2.1 Physical characteristics of aggregates.

For the elaboration of concrete mixtures was used the method of the ACI 211.1 [11], the first stage is the characterization of the physical properties of aggregates (fine and coarse) to use, these features are used in this method to reach the ideal dosage for a concrete according to the specific requirements requested. Of the above the Table1 summarizes the physical characterization of materials used in this research. The tests were performed according to ONNCCE standards.

Table 1. Physical characteristics of aggregates used in the mix

Physical Property	Coarse Aggregate	Fine Aggregate
Specific Gravity (gr/cm ³)	2.32	2.66
Dry-roddedweith (kg/cm ³)	1380	- - -
Absorption (%)	4	3.8
Fineness Modulus	- - -	2.7
Maximum Aggregate Size (inch)	³ / ₄	- - -

2.2 Proportioning of concrete mixture.

For this work was used Portland cement type CPC 30R [12] and drinking water. To obtain the dosage or the proper proportioning of the materials from which the concrete is made (cement, water, fine and coarse aggregates) to prepare the mixture and with it make the specimens for study. It was used the method of ACI 211.1, methodology that is based on considering the physical properties of aggregates. According to the characteristics of the materials and the desired resistance to compression of $f'c=250\text{kg/cm}^2$, the proportioning was calculated as shown in the Table 2.

Table 2. Proportioning of concrete mixtures (for 1 m³)

Materials (kg)	$f'c=250\text{kg/cm}^2$
Water	205
Cement	311
Coarse Aggregate	869.40
Fine Aggregate	959.40

2.3 Characterization of concrete in fresh and hardened state.

To determine the characteristics of concrete in fresh and hardened state (resistance to compression), assays were performed according to the standards ONNCCE. The tests and results of them are listed in Table 3.

2.3 Characteristics of the specimens and electrochemical tests

The specimens are made with four mixtures each with different degrees of contamination, one of them without the addition of NaCl and the other three with an addition to the mixture of 2, 3 and 4% of NaCl respect to the weight of cement, this to simulate concrete where the chlorides are incorporated into the concrete from elaboration, is for this reason they present seawater, sea sand, additives, and so forth. The specimens were exposed to a simulated marine environment with a 3% solution of NaCl during 365 days.

Table 3. Physical and mechanical properties of employees concrete

Test	$f'c=250\text{kg/cm}^2$
Slump (NMX-C-156-1997-ONNCCE) [13]	7 cm
Temperature (ASTM C 1064 / C1064M - 08) [14]	22 °C
Density (NMX-C-105-ONNCCE-2010) [15]	2150 kg/m ³
Mechanical strength (NMX-C-083-ONNCCE-2002) [16]	25.0 MPa

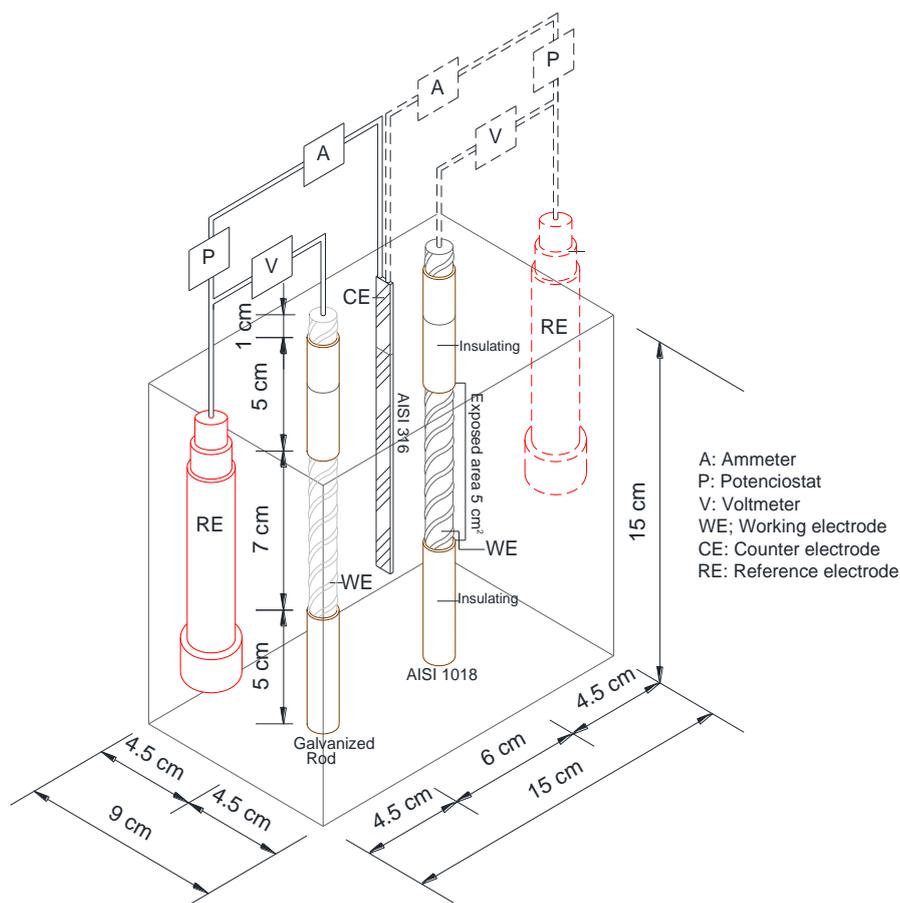


Figure 1. Scheme of the prismatic specimen used.

For the specimens under study and according to the parameters to value, was proposed nomenclature which is shown in Table 4.

Table 4. Nomenclature

Serie EL				Serie EZ			
EOZ	E2L	E3L	E4L	EOZ	E2Z	E3Z	E4Z
Z = Galvanized Rod L = AISI 1018				0 = Clean Concrete 2 = Contaminated Concrete(2% NaCl) 3 = Contaminated Concrete(3% NaCl) 4 = Contaminated Concrete(4% NaCl)			

For electrochemical evaluation of the galvanized bars and AISI 1018 steel was carried out the corrosion potential (E_{corr}) monitoring according to the standard ASTM C876-99 [17] and the kinetics or rate of corrosion with the technique of linear polarization resistance (LPR). The data were collected with a sweep ± 20 mV vs. E_{corr} and a sweep rate of 10 mV /min. the equipment was used for these tests was a Gill AC potentiostat/galvanostat/ZRA ACM instruments with a reference electrode of copper-

copper sulfate (Cu/CuSO₄). The experimental arrangement shown in Figure 1, where: AE=auxiliary electrode (ASI 316), WE=working electrode, RE=reference electrode Cu/CuSO₄ and 3% NaCl=solution to 3% in NaCl.

The corrosion potential monitoring of the test specimens was performed according to ASTM C876-99 standard, and evaluation were carried out according to what shown in Table 4.

Table 4. Corrosion Potentials E_{corr} (mV vs Cu/CuSO₄) [18].

E _{corr} (mV vs Cu/CuSO ₄)	Probability of Corrosion
< - 500	Severe Corrosion
-500 to -350	90% Probability of Corrosion
-350 to -200	Uncertainty of Corrosion
> -200	10% Probability of Corrosion

3. RESULTS

3.1. Corrosion potentials

The Figure 2 shows the results of E_{corr} of galvanized steel specimens. Is observed that the degree of contamination of the mixture influences for potentials of the three specimens contaminated with 2, 3 and 4% of NaCl are under -500 mV from the curing stage indicating the initiation of a severe corrosion, and that only the specimen prepared with clean concrete and galvanized steel (E0Z) presents which over time is located in the zone of 90% probability of corrosion, with a tendency to the zone of uncertainty, also presented a better behavior up to 120 days of exposure, however, is observed to stabilize up to 365 days in severe corrosion.

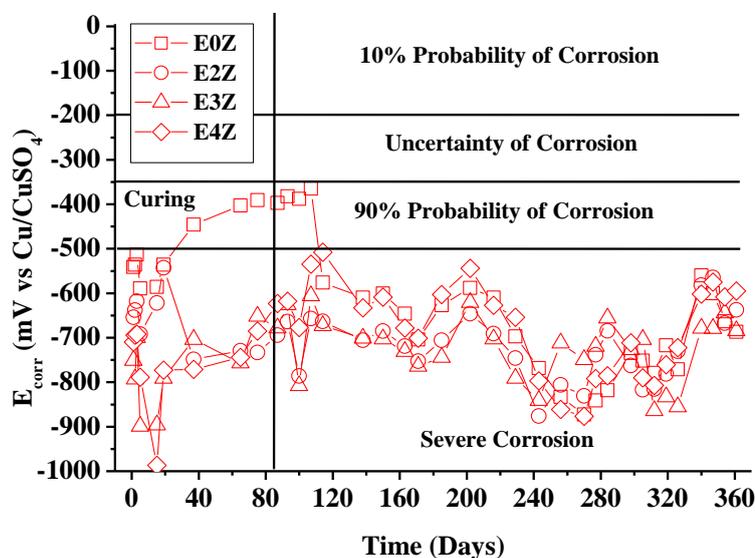


Figure 2. Corrosion potential (E_{corr}) versus time (days) for specimens with galvanized steel.

Figure 3 shows the results of E_{corr} of the specimens with AISI 1018 steel. It is observed that both: the clean concrete specimen (E0L) as specimens with 2, 3 y 4% of NaCl present E_{corr} values lower than -350 mV, which indicates a 90% probability of corrosion. Not observed at the end there is a difference in vulnerability to corrosion of steel AISI 1018 to be or not contaminated concrete and exposed to a marine environment. Between 280 and 340 days, specimens E2L, E3L and E4L are located in severe corrosion potentials.

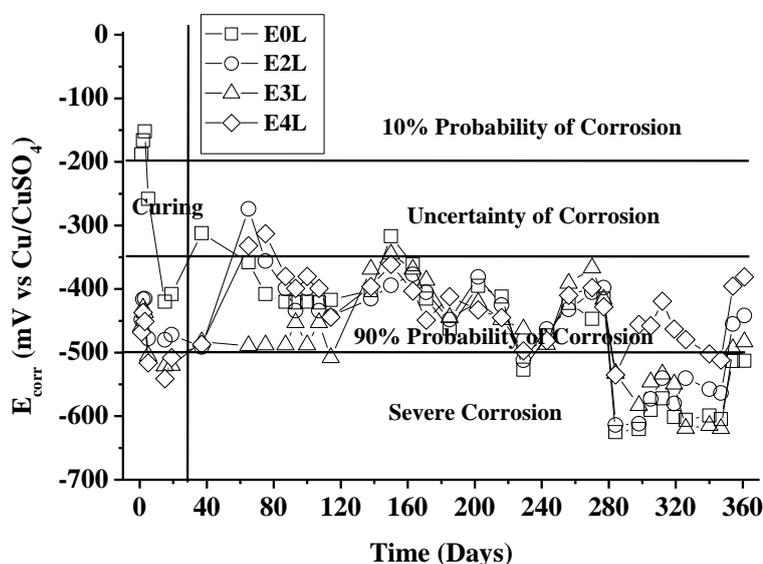


Figure 3. Corrosion potential (E_{corr}) versus time for specimens with AISI 1018 steel.

3.2 Linear polarization resistance

The interpretation of values of i_{corr} was performed as indicated in the manual of Durar network, which indicate the level of corrosion according to this value, as shown in Table 5.

Table 5. Corrosion levels were defined according to the Durar Network Specifications [19]

Corrosion Rate (i_{corr}) $\mu\text{A}/\text{cm}^2$	Corrosion level
< 0.1	passivity
0.1 – 0.5	low corrosion
0.5 – 1	high corrosion
> 1	very high corrosion

The Figure 4 presents the results of the corrosion rate (i_{corr}) of specimens with galvanized steel bars embedded in clean concrete and concrete with different degrees of contamination in the mixture in 2, 3 and 4% of NaCl, is observed the galvanized steel bar is embedded in a clean concrete (in terms of construction well developed) without contaminants in the mixture (E0Z), the galvanizing behaves with

great performance in a marine environment with values of i_{corr} under $0.1 \mu A/cm^2$ until 150 days of exposure, indicating a negligible corrosion or passivity, after this period i_{corr} values increased to $1.1 \mu A/cm^2$, to locate in high corrosion. The E2Z specimen shows moderate corrosion until day 150, increased after this period in high corrosion. But the bars embedded in concrete contaminated with 2 and 4% of NaCl (E3Z and E4Z) showed high corrosion from the curing period until the end of exposure.

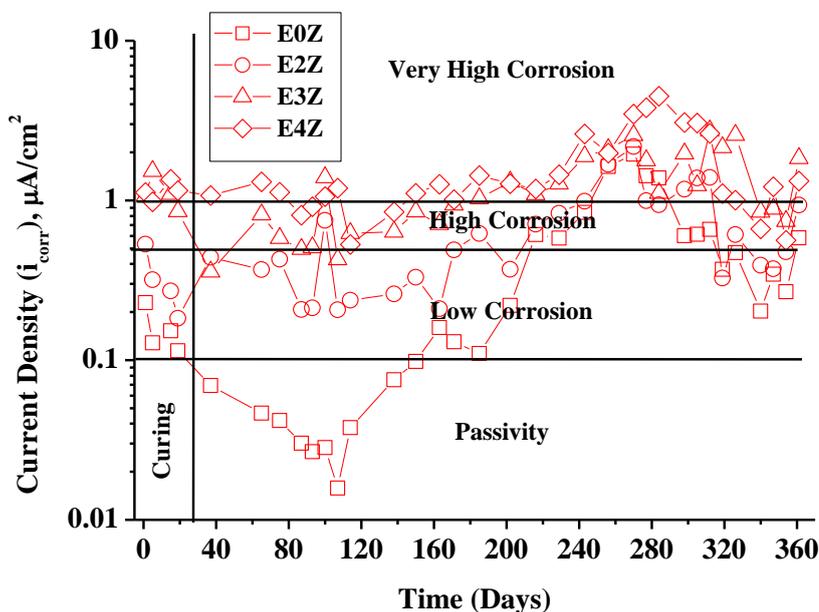


Figure 4. Corrosion rate (i_{corr}) versus time (days) for specimens with galvanized steel.

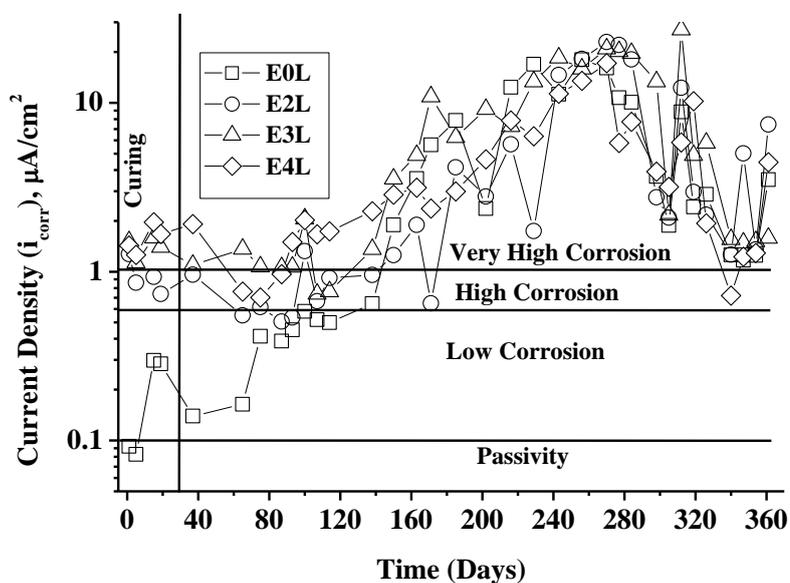


Figure 5. Corrosion rate (i_{corr}) versus time (days) for specimens with AISI 1018 steel.

In contrast to Figure 4, in the Figure 5 shows that the corrosion rate in specimens of AISI1018 steel is higher, and the clean concrete specimen including magnitudes of corrosion rate (i_{corr}) above $0.5 \mu\text{A}/\text{cm}^2$ after 120 days of exposure which is considered high corrosion, also distinguishes the effect of NaCl percentage. Where the specimens with highest percentage of contamination (to which was added the 3% and 4% of NaCl) present very high corrosion at 180 days. Is observed the fastest rate of corrosion, decreasing values of i_{corr} until day 340, with values between 1 and $5 \mu\text{A}/\text{cm}^2$.

4. DISCUSSION

To better understand the behavior of specimens with galvanized bars and AISI-1018 steel bars, the graphics are presented with the results of corrosion potentials (E_{corr}) and corrosion rate (i_{corr}) which demonstrates the low protection provided by a galvanized steel bars embedded in concrete contaminated with NaCl.

To perform a corporative analysis of corrosion potential (E_{corr}) of specimens with galvanized bars and AISI 1018 steel bars, as shown in the Figure 6 is observed that the potentials that the potentials of specimens with galvanized bars shown lower values than AISI 1018 steel bars, this is attributable to zinc is more electronegative than the steel in the galvanic series and, in particular, the corrosion potentials corresponding to “active state” and “passive state” of the zinc coatings with reference to the “decomposition line of water” in the zinc Pourbaix’s diagram are known [20].

Although the EZ0 specimen presents corrosion potential values of -700 mV and even lesser than -400 mV to clean concrete specimen, this according to literature that indicates a severe corrosion and 90% probability of corrosion respectively.

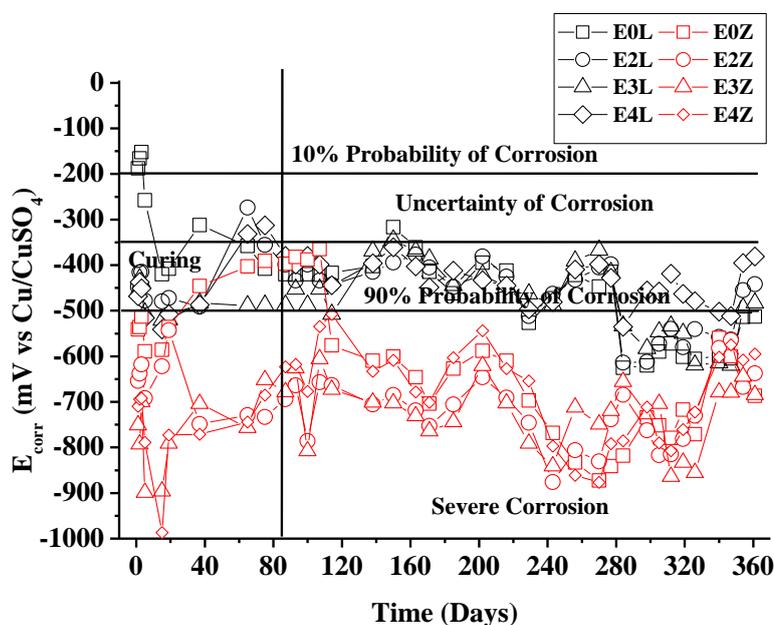


Figure 6. Comparison (Potential corrosion) of specimens with galvanized steel versus AISI 1018 steel

The specimens that showed better behavior in the marine environment were E0Z and E2Z with negligible and moderated corrosion respectively, this is observed in Figure 7, where can be observed like all the other, including the E0L specimen of clean concrete and AISI 1018 steel, presents high corrosion, also can be noted that AISI 1018 steel specimen present a high corrosion rate than specimens with galvanized bars. But the behavior of zinc is not very efficient, because the corrosion rate was also very high. Is necessary to distinguish clearly the formation of self-protective layer of zinc corrosion products (zinc oxide, basic carbonates) that were formed during the curing stage until approximately 160 days of exposure, when i_{corr} was low, and the unstable layer of zinc hydroxide (hydroxide and hydrated oxides) that are products generated by the phenomenon of white zinc corrosion. The products generated in this condition are white and porous spots which consisted in $2ZnCO_3 \cdot 3Zn(OH)$ and ZnO [21], which caused the protection of zinc was lower while the concrete contamination with NaCl was bigger. The zinc– iron reactivity is mainly influenced by the silicon and phosphorus steel content. It is noteworthy that the chlorides concentration thresh- old necessary for the attack initiation on the galvanized bar embedded in specimens was in all cases significantly higher than that reported in the literature [22,23,24,25].

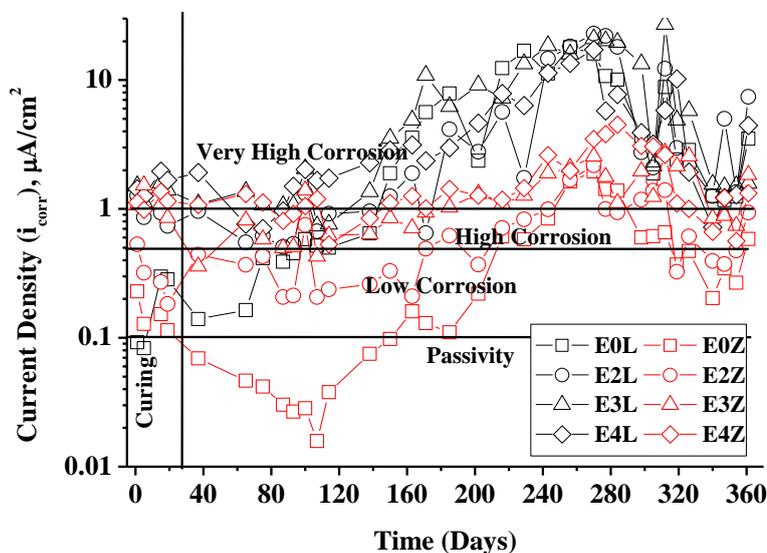


Figure 7. Comparison (i_{corr}) of specimens with galvanized steel versus AISI 1018 steel

5. CONCLUSIONS

The results of this research demonstrate the importance of caring for the material for the production of concrete, because was shown that the best performance of steel as corrosion protection in concrete exposed in marine environments occurs when the concrete is free of chlorides from elaboration, since, as was observed at concentrations above 2% of NaCl in the mixture of concrete, galvanized steel bars embedded in contaminated concrete, also in marine environment, corrode with

the same intensity as the steel-1018, although corrosion will attack the coating due to the level introduced in this study, does not comply with the mission to increase the service life of concrete structures under this conditions .

The use of zinc is adequate, provide the concrete is not contaminated or with a presence of relative humidity greater than 80%, since the corrosion of zinc can not be reduced to a problem simply aesthetic, because these types of products are indicative of corrosive attack on the protective layers of steel, for this reason is necessary to give adequate treatment to counter the possible loss of the zinc layer, which is to provide protection to the steel by extending the useful life of the base material and retarding corrosion.

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References

1. M. A. Baltazar-Zamora (et. al.), *Portugaliae Electrochimica Acta*, 27, (2009) 237
2. M. A. Baltazar-Zamora (et. al.), *Scientia et Technica*, 36, (2009) 353
3. T.Belleze et. al., *Cement Concrete Comp*, 28, (2006) 246
4. A.R., Frías, , “Mantenimiento y Conservación de Puentes”, Secretaría de Comunicaciones y Transportes, México (2010)
5. Yeomans SR, editor. Galvanized Steel Reinforcement in concrete Oxford: Elsevier Science Ltd; (2004)
6. D. A. Whiting, M. A. Nagi and J. P. Broomfield, 52, 6, (1996) 472-479.
7. W. H. Hart, NACE Corrosion Congress Paper No. 252. (1997),
8. T. Bellezze, M. Malavolta, A Quaranta, N Ruffini, G. Roventi, *Cement Concrete Comp*, 28, 3 (2006) 246-255
9. Obada Kayali, Stephen R. Yeomans, *Cement Concrete Comp*, 22 (2000) 459-467
10. Rita Ghosh, D.D.N. Singh, *Surf Coat Tech*, 201, 16–17, (2007) 7346-7359
11. ACI. Proporciónamiento de Mezclas, Concreto normal, pesado y masivo ACI 211.1, p. 29. Ed. IMCYC, México (2004).
12. NMX-C-414-ONNCCE-2004 Standard, Cementos Hidráulicos -Especificaciones Y Métodos De Prueba, ONNCCE S. C., México (2004).
13. NMX-C-156-1997-ONNCCE Standard, Determinacion de Revenimiento en Concreto Fresco, ONNCCE S. C. ,Mexico (1997).
14. ASTM C 1064 / C1064M – 08 Standard, Standard Test Method for Temperature of Freshly Mixed Hydraulic-Cement Concrete. American Society for Testing and Materials, USA (2008).
15. ONNCCE S. C. NMX-C-105-ONNCCE-2010 Standard, Concreto Hidraulico Ligero Para Uso Estructural-Determinacion de la Masa Volumetrica ONNCCE S. C., Mexico (2010)
16. NMX-C-083-ONNCCE-2002 Standard, Determinación de la Resistencia a la Compresión de cilindros de concreto - Método de prueba, ONNCCE S. C., Mexico (2010)
17. ASTM C 876-99 Standard, Test Method for Half-cell Potentials of Uncoated Reinforcing Steel in concrete, American Society for Testing and Materials, (1999).

18. H. Won-Song and V. Saraswathy., *Int. J. Electrochem. Sci.*, 2, 1 (2007).
19. Red DURAR, Manual de Inspección, Evaluación y Diagnóstico de Corrosión en Estructuras de Concreto Armado, CYTED Program, Rio de Janeiro, (1997).
20. A. Macias, C. Andrade. *Br Corros J* ,3, 22(1987)162-71. Red DURAR, Manual de Inspección, Evaluación y Diagnóstico de Corrosión en Estructuras de Concreto Armado, CYTED Program, Rio de Janeiro, (1997).
21. R.W. Richards, H. Clarke. The influence of steel surface characteristics on galvanizing reactivity. EGGA, editor. Proceedings of the 17th international galvanizing conference. Paris: EGGA (1994) GC7/ 1-GC7/12.
22. R. Fratesi *Industria Italiana del Cemento*, 735(1998) 720-33.
23. P. Pedferri, L. Bertolini. La corrosione nel calcestruzzo e negli ambienti naturali. Milano: McGraw-Hill; (1996).
24. Yeomans SR. *Corrosion*; 50 (1994) 72-81.
25. Nieves M.D., Almeraya C.F. (et al) *Corrosion* No.12 Vol. 64 pp 920-928