



Resistance of Anticorrosive Coatings on Carbon Steel in Nine Cities of Ecuador

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ARTICLE INFO

Article history:

Received: 02 Apr 2021

Final Revised: 28 Aug 2021

Accepted: 30 Aug 2021

Available online: 29 Nov 2021

Keywords:

Atmospheric corrosion

Inorganic coatings

Galvalume

Magnelis

Zinc-based coatings.

ABSTRACT

This study shows the protection level of various anticorrosive coatings applied on carbon steel through laboratory and field tests performed in a salt spray test chamber and a xenon arc testing machine for up to 500 hours. Field tests developed them during one year in nine cities of Ecuador (South America). Quito (two urban stations), Guayaquil (one station marine and another urban-marine), Santo Domingo (subtropical station), Manta (urban-marine), Portoviejo (urban), Machala (urban-marine), Latacunga (urban), Cuenca (industrial), and Esmeraldas (industrial-marine). Field tests allowed it to determine the corrosive category of these cities. The stations from Esmeraldas and Cuenca presented the most aggressive environments. In this first-year study, the results obtained with these coatings evidence their behavior depends on the test station. This behavior explained remarkable differences in marine, industrial, mixed locations and those with high relative humidity. Prog. Color Colorants Coat. 15 (2022), 213-223© Institute for Color Science and Technology.

1. Introduction

The study of the atmospheric deterioration of engineering materials is critical, and it allows determining essential aspects of engineering; among these stand out the proper design of industrial equipment and pipes, the lifespan of the materials, protection necessities, the risks in metal structures exposed to the outside environment, etc. [1]. Approximately 4 to 5 % of losses for a country's gross domestic product are attributed to metallic corrosion; moreover, around 50 % of them correspond to atmospheric corrosion [2, 3].

A prevalent way of protecting metallic materials like carbon steel has been through zinc-based coatings. An example of this is galvanized Steel, yet its resistance in specific aggressive environments has been unsatisfactory. For this reason, other metallic coatings have been formulated to improve resistance and reduce their thickness [4]. Other used coatings have a

polymeric origin, such as resins: alkyd, acrylic, polyurethane, polysiloxane, epoxy, polyamides, and polybenzoxazine [5-9]. Zinc-based metallic coatings have a broad range of commercial options. Among them: Galvalume® and Magnelis®, as the most relevant, it has been shown that both commercial materials have an excellent response to corrosion. This material can be attributed to the formation of aluminum, zinc, and magnesium in the Magnelis® as protective products. Altogether increases the protection of the base metal by suppressing the formation of zinc oxide (ZnO), a product that provides less protection [10]. However, their response against corrosion has been tested in various atmospheres. These metallic coatings have not been tested in previous experiments in Ecuador [11].

The application of paints on metallic materials is a versatile alternative for anticorrosive protection. Thus, there are materials provided with one or more layers of

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paint, varnishes, and a metallic coating. These offer good resistance to corrosion of metallic structures in a variety of atmospheric environments [12].

The behavior of anticorrosive coatings in atmospheric environments depends on many factors, and it is strongly dependent on the geographic exposure location. It determines the need to develop natural exposure tests at the location sites of interest [13]. The first study of atmospheric corrosion in Ecuador was carried out in 1998 by the "Iberoamerican Map of Atmospheric Corrosivity" project, MICAT, where corrosion and contamination values were obtained in five Ecuadorian cities [14]. Besides, the previous studies have considered neither the extension of all the cities analyzed here nor the anticorrosive materials used (zinc exception).

Thus, the present study analyzes the resistance of various coatings to atmospheric corrosion in nine cities of the country based on their productive, economic, and social importance. Such as Quito, Guayaquil, Santo Domingo, Manta, Portoviejo, Esmeraldas, Cuenca, Latacunga and Machala. Quito and Guayaquil have located two stations in each one, in the cities of Manta, Machala, Cuenca, and Latacunga; there are no previous studies of contamination or atmospheric corrosion.

2. Experimental

2.1. Determination of the atmospheric aggressiveness of stations

The atmospheric aggressiveness of the analyzed stations was determined utilizing standardized field tests of metallic exposure of carbon steel. Also, the meteorological and pollution variables were measured with the final objective of adequately characterizing the stations in each city.

2.2. Standardized metal exposure field tests

Several cities considered the economic and industrial importance of the country were selected and listed in Table 1. Where DASL is the distance above sea level. Low carbon steel samples with 1.1 mm thickness were analyzed. Two samples were extracted every three months until completing one year according to ASTM standards [15, 16]. First, samples were cleaned with an organic solvent. Then, they were exposed and extracted according to the established times. Through photographic recording and optical microscopy, it was determined the type of corrosive attack that samples had. At the same time, the pollutants and types of corrosion were characterized by X-ray diffraction (XRD) in the Norelco Philips D2 Phaser equipment.

Table 1: Exposure sites considering the studied cities.

City	Code	DASL (m)	Longitude	Latitude	Type of station
Santo Domingo	SD	625	79°12'23.7"W	0°13'56.9"S	Subtropical
Guayaquil (center)	G1	4	79°56'06.5"W	2°06'12.3"S	Urban Marine
Guayaquil (Seaport)	G2	4	79°52'37.1"W	2°08'56.6"S	Marine
Portoviejo	P	53	80°27'24.0"W	1°02'29.5"S	Urban
Quito (North center)	Q1	2850	78°29'44.8"W	0°11'03.6"S	Urban
Quito (South center)	Q2	2850	78°29'19.9"W	0°12'36.2"S	Urban
Latacunga	L	2750	78°36'54.9"W	0°47'23.3"S	Urban
Machala	MC	12	79°58'34.3"W	3°15'10.1"S	Urban Marine
Manta	MN	6	80°44'43.8"W	0°57'05.4"S	Urban Marine
Cuenca	C	2560	78°58'23.6"W	2°52'54.0"S	Industrial
Esmeraldas	E	15	79°40'36.2"W	0°55'50.2"N	Industrial Marine

The quantification of the corrosion degree of the carbon steel samples was done by Equation 1. G is the degree of corrosion ($\mu\text{m} / \text{year}$, when the corrosion is uniform), W is the lost weight of the material (g), T is the exposure time (h). Also, B is the test tube area (cm^2), D is the density of the material (g / cm^3), and K is the constant that expresses the degree of corrosion.

$$G = (K W) / B T D \quad (1)$$

The loss of thickness or mass of the test tubes (gravimetric measurements) was evaluated with this equation according to the ASTM G1-03 standard [13].

2.3. Pollution tests and meteorological variables

The concentration level of sulfur dioxide pollutants and nitrogen oxide and chlorides (in the case of stations near the sea) were obtained with the equipment of the "Secretaría del Ambiente de Quito". The degrees of corrosion obtained and the meteorological variables monitored during the year were used to classify the selected cities by the ISO 9223 standard [18].

2.4. Evaluation of the protection level of coatings

The evaluation was carried out through two corrosion tests: field exposure and laboratory.

2.4.1. Standard metal exposure field tests

The samples of Galvanized Steel, Galvalume, magnelis, and galvanized Steel coated by an acrylic resin were tested in the anticorrosive coatings. Table 2 lists the specifications of each material.

Coating samples were exposed in the areas described in Table 2 and complied with the parameters established in the ASTM G50 and ISO 8565 standards in the analysis periods of 3, 6, 9, and 12 months. A photographic record of all samples and microscopic analysis was carried out at the end of 12 months.

2.4.2. Protection level assessment: metallic coatings

The degree of corrosion of the coating was obtained using gravimetric measurements under the ASTM and ISO standards [18, 19]. This measurement helps to determine the level of anticorrosive protection of these coatings. Similarly, with the carbon steel, the samples were weighed with the SHIMADZU AUX220 analytical balance (± 0.0001 g) and proceeded according to the stipulations of the mentioned standards.

2.4.3. Protection level assessment: polymeric coating

The degree of deterioration and types of failures of the coating samples were evaluated based on ISO 4628 standard through visual and microscopic inspection of the exposed test tubes over scales and photographic patterns [20]. Additionally, an infrared spectrophotometry analysis was performed, using the attenuated total reflectance (ATR) technique with the Perkin Elmer Spectrum One FTIR, which allows early warning of the degree of degradation and identifies its causes, chain breakage, charge migration, etc.

Table 2: Specifications of Anticorrosive Coatings.

Material	Coating Thickness (μm)	Composition (%)			
		Zn	Al	Mg	Si
Galvanized	98.0	99.8	0.2	-	-
Galvalume	26.0	43.4	55.0	-	1.6
Magnelis	13.0	93.3	3.7	3.0	-
Polymeric Coating	25.0	Acrylic thermoset			

2.4.4. Standard laboratory tests

The Q-Fog CCT-600 Salt Spray Chamber was used with the conditions established by standards ASTM B117 (marine environment) and ASTM G85 (industrial environment) [21, 22]. A total of 500 hours was tested for each trial. The analysis of the samples' deterioration proceeded similarly as in the field tests.

Also, the polymeric coating has been tested for a total of 500 hours with a conventional cycle through Xenon Arc Chamber Q-SUN XE-1-S by using the standard ASTM D6995. This test showed the capacity of this material to resist the deterioration of its properties in the face of exposure to solar light, temperature, and moisture [5, 24].

3. Results and Discussion

3.1. Categorization of the atmospheric aggressiveness of stations

Table 3 presents the corrosion result of carbon steel at the end of one year in all the stations. The meteorological and pollution variables are indicated. Also, The rugosity values and the main corrosion products: Lepidocrocite (L), Goethite (G), Akaganeite (A), were determined. Based on these results, the corresponding ISO 9223 category is established for each city: Corrosivity (C), Pollution (P), Salinity (S), and Wetting Time (TDH), the subscripts reflect the degree of intensity from the evaluated variable in each ISO category.

The results show that carbon steel had more

significant losses in the marine-industrial atmosphere of Esmeraldas due to the synergistic effect of gaseous pollutants and the salinity characteristic of these environments. The city of Cuenca also has a very high corrosion value since the station was in the Industrial Park, where there are many industrial companies. Guayaquil, influenced by the proximity to the sea and vehicular traffic, presents average corrosivity values. While the cities of Manta and Machala, both coastal cities, have corrosion levels somewhat lower than Guayaquil due to less vehicular traffic. The Latacunga station lies close to the Cotopaxi volcano, which has emitted gaseous emissions throughout the year, although they were not very significant. The Santo Domingo station is in a sector with low traffic flow but high humidity. These corrosiveness values are like the Quito and Portoviejo stations, urban atmospheres with a higher level of traffic.

As observed in Figure 1, the corrosion rate for each station functions a time for the first year of exposure. In all cases, the decrease in this rate can be seen as the corrosion layer grows on the metal plate; in the most aggressive atmospheres, this decrease is more evident because the initial attack is higher.

Also, Figure 2 shows the corrosion produced on carbon steel in industrial, marine, and urban stations through optical microscopy inspection during the first year of exposure where the main corrosion products were Lepidocrocite (L), Goethite (G), as before explained.

Table 3: Characterization of the tested cities during the year of study.

Station Code	Corrosion of carbon steel (μm)	Category corrosivity ISO	Pollution degree ISO SO_2	Pollution degree ISO Chlorides	Wetting Time ISO	Corrosion Products
Q1	7.3	C ₂	P ₀	S ₀	T ₄	L, G
P	8.7	C ₂	P ₀	S ₁	T ₅	L, G
Q2	9.7	C ₂	P ₀	S ₀	T ₄	L, G
SD	9.7	C ₂	P ₀	S ₀	T ₅	L, G
G1	14.5	C ₂	P ₀	S ₁	T ₄	L, G
MN	20.3	C ₂	P ₁	S ₂	T ₅	L, G, A
L	21.3	C ₂	P ₁	S ₀	T ₄	L, G
MC	21.6	C ₂	P ₁	S ₁	T ₄	L, G
G2	22.8	C ₂	P ₁	S ₁	T ₄	L, G
C	41.9	C ₃	P ₁	S ₀	T ₄	L, G
E	51.8	C ₄	P ₂	S ₁	T ₅	L, G

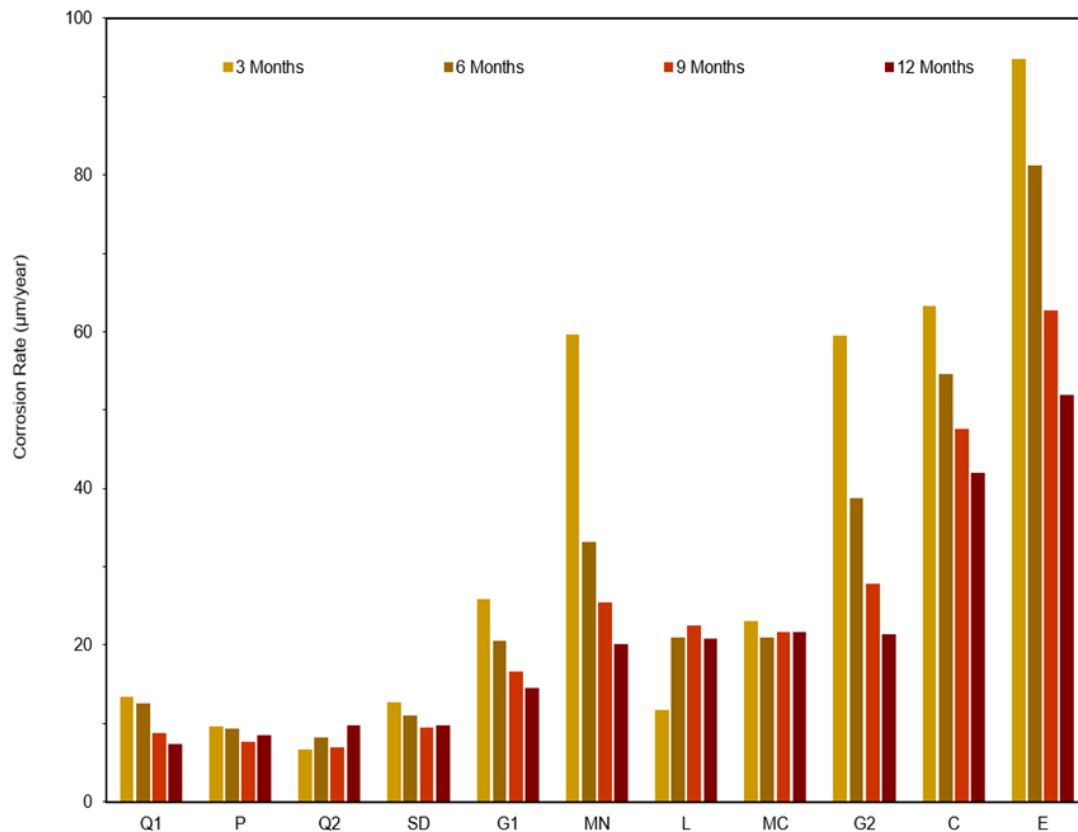


Figure 1. The corrosion rate of carbon steel during the year of study in the tested cities.

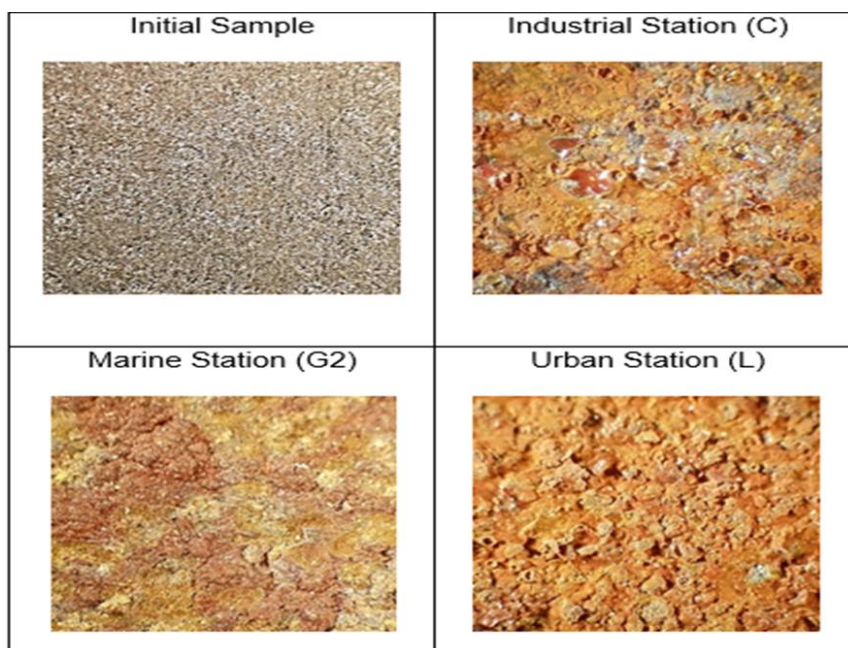


Figure 2. Optical microscopy inspection of corrosion products on carbon steel at the year in industrial, marine, and urban stations of study

3.2. Evaluation of metallic coatings

3.2.1. Field tests

The loss result of material as a function of time and comparison after one year are presented in Figure 3. This fall occurs due to the corrosion of the respective coatings. After one year of exposure, some important conclusions can be drawn. As can be seen in Figures 3a and d, zinc coating had more significant thickness losses in industrial areas with high levels of contamination (Cuenca). In those cities where there were high wetting times, such as Santo Domingo and Esmeraldas, too. In the stations with less SO₂ pollution and those close to the sea, thickness losses are lower. This result can be explained because zinc forms zinc oxide, hydroxide, and carbonate in the atmosphere, and a high concentration of SO₂ can dissolve them and end their protective effect. Still, this dissolution is

counteracted if chloride ions are present in the surrounding atmosphere. The increase in the surface pH because of chloride ions allows the formation of relatively protective corrosion products. At the same time, it considerably attenuates the corrosion rate [14, 25]. According to ISO regulations, Cuenca, Santo Domingo, and Esmeralda's stations correspond to category C₃ and the other ones to C₂.

Galvalume corrodes to a greater extent in marine atmospheres (Guayaquil and Manta) than in industrial and urban atmospheres, as shown in Figures 3b and d. In aquatic environments, chloride ions attack aluminum producing non-protective oxides [26]. This behavior is ratified in several studies of the material. Where higher corrosion values are showed in those areas with the highest concentration of chloride ions [27].

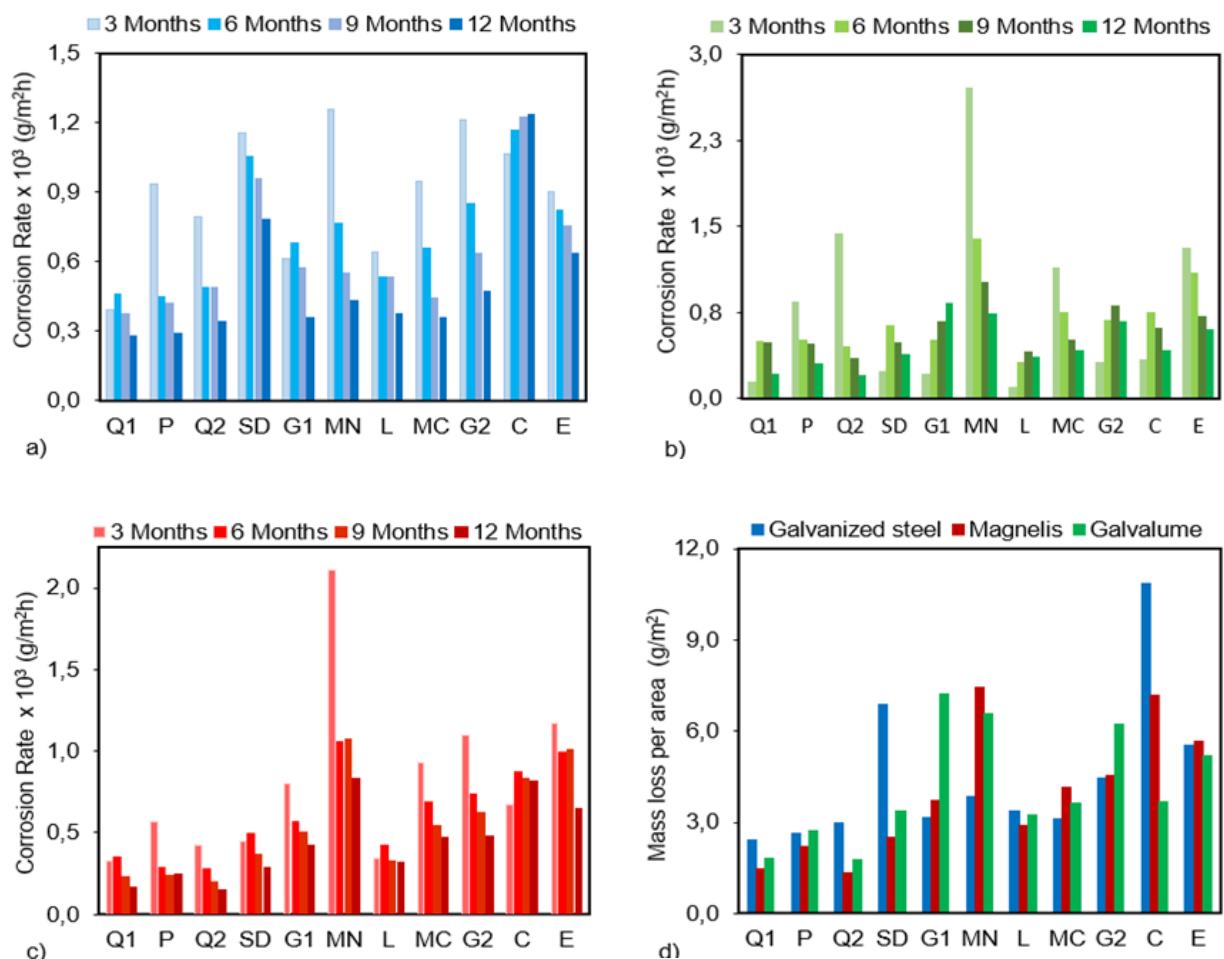


Figure 3: a) Corrosion rate of galvanized Steel, b) galvalume, c) magnelis and d) one year of study and its corrosion comparison, at the end of the year in the tested cities.

In the case of magnelis, it is noted that there are more significant losses in Esmeraldas and Cuenca, related to the long-term studies of magnelis that show a greater loss of thickness in marine areas with substantial industrial pollutants [28]. It presents a better resistance in urban environments and very humid uncontaminated environments (such as Santo Domingo) [29].

Moreover, Figure 4 shows the corrosion produced on metallic coatings analyzed in industrial, marine, and urban stations through optical microscopy inspection during the first year of exposure. It could see the corrosion made in each material, as previously said. The presence of particulate matter was the reason for corrosion in the case of the industrial station.

3.2.2. Laboratory tests

Table 4 shows the results of the trials after 500 hours of testing for each of the ASTM standards. Corrosion

losses of zinc are always more significant than other systems; when the test is carried out, this coincides with the environmental results. The loss of thickness in the ASTM B117 test (which has a higher percentage of chloride ions) is very high; it is possible because of the characteristics of the test (not cyclical as it happens in the outside atmosphere); thus, protective oxides are not formed. In the case of Galvalume, there is a more significant loss of thickness compared to the G85 test. This loss determined the presence of chlorides in the B117 test and corresponded to what happens in the outdoor environment. In the case of Magnelis, the difference in thickness loss is not more significant between the two tests. In general, once the cyclical characteristics of the G85 test are given, it can expect that it better represents what happens in external atmospheric corrosion.

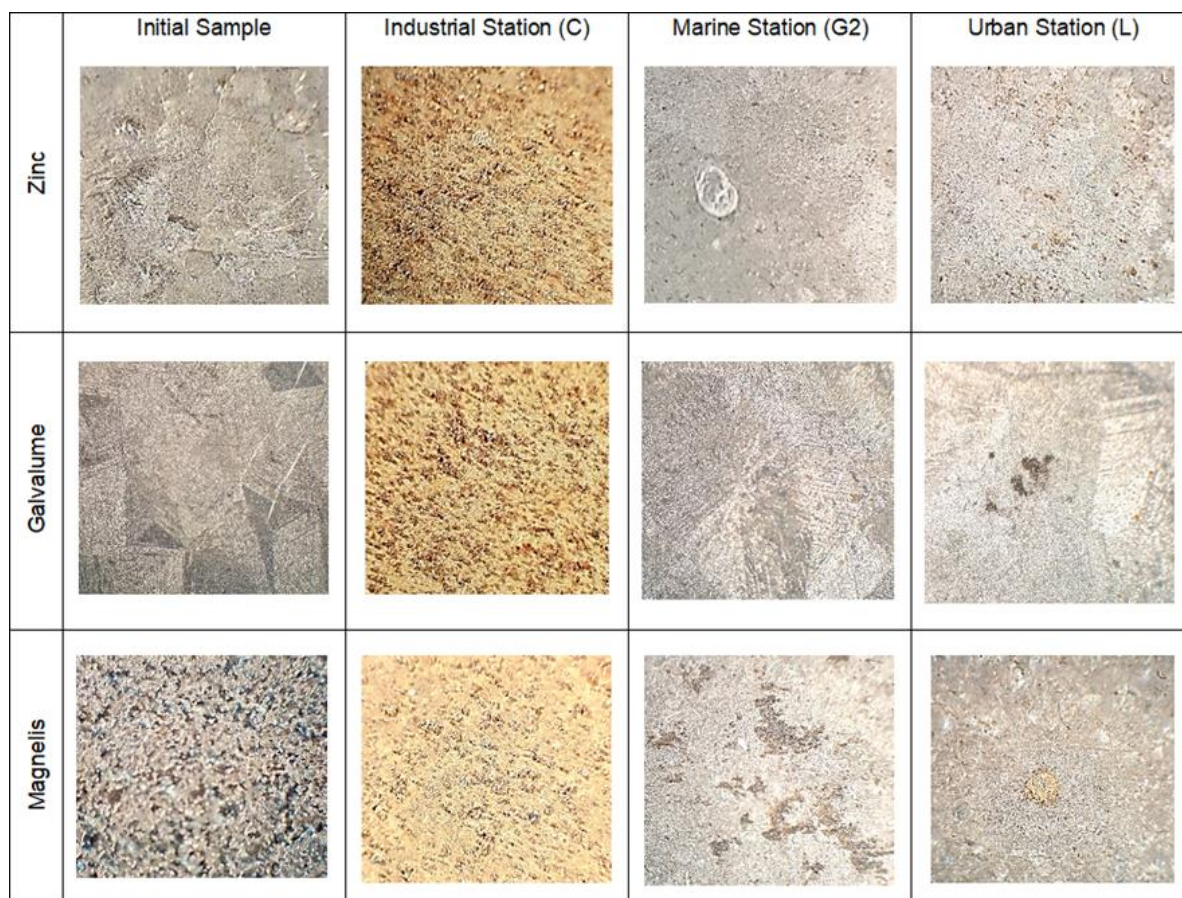


Figure 4: Optical microscopy inspection of metallic coatings at the year in industrial, marine, and urban stations of study.

Table 4: Loss of thickness after 500 hours.

Material	ASTM B117 Loss of thickness (g/m ²)	ASTM G85 Loss of thickness (g/m ²)
Galvanized	80	40
Galvalume	30	7
Magnelis	30	28

3.3. Evaluation of polymeric coating

3.3.1. Field tests

The samples of the polymeric coating analyzed over a year show a degree of oxidation and a slight color change; also, they did not present other imperfections such as cracks, blisters, flaking, or plastering. Table 5 reports the results of the degree of oxidation that occurred in the test stations. The highest values recorded are in Cuenca and Esmeraldas, attributed to these stations' highest pollution values. In the case of Cuenca, the presence of abundant particulate material was relevant too.

According to those mentioned above, it is evident at an atmosphere like that obtained in Cuenca; the coating

has more excellent effects on its surface and visual structure. But, in atmospheres such as Machala, Manta, and Guayaquil (Santa Leonor), it has very few results. The polymeric samples were analyzed in a microstructural way on FTIR tests by monitoring the carbonyl group (CO) band. In cities such as Esmeraldas and Santo Domingo, they showed more significant coating degradation at the end of one year. Similarly, high levels of relative humidity in both places presumably caused this behavior. On the other stations, this degradation was moderate. It could be observed with the comparison of the carbonyl group band before its exposure (a) and at the end of the study year (b), which may be seen in Figure 4 (Santo Domingo station).

Table 5: Most remarkable degree of deterioration in field trials.

Station	Degree of oxidation %
C	2.50
E	1.00
SD	0.50
Q1	0.50
Q2	0.50
G1	0.50
L	0.50
P	0.50
MN	0.05
MC	0.05
G2	0.05

3.3.2. Laboratory tests

In the tests carried out in a Salt Spray Test Chamber, no essential differences in the results were observed with both the ASTM B117 and ASTM G85 standards. There were two types of defects in both cases: slight color change and blistering, which after 500 hours, corresponding to a grade 2 (S₂) according to the ISO 4628 standard.

No notable physical changes were observed in the 100, 300 and 500 hours tested in the xenon arc chamber tests. The FTIR analysis showed the degradation process of the first use. This degradation was based on the continuous formation of perhydroxide and hydroxyl groups in the exposure time. At the same time, it generates a general tendency to increase the carbonyl group, which corroborates the trend obtained on the field trials similarly. Figure 5 shows the trend reflected in the laboratory.

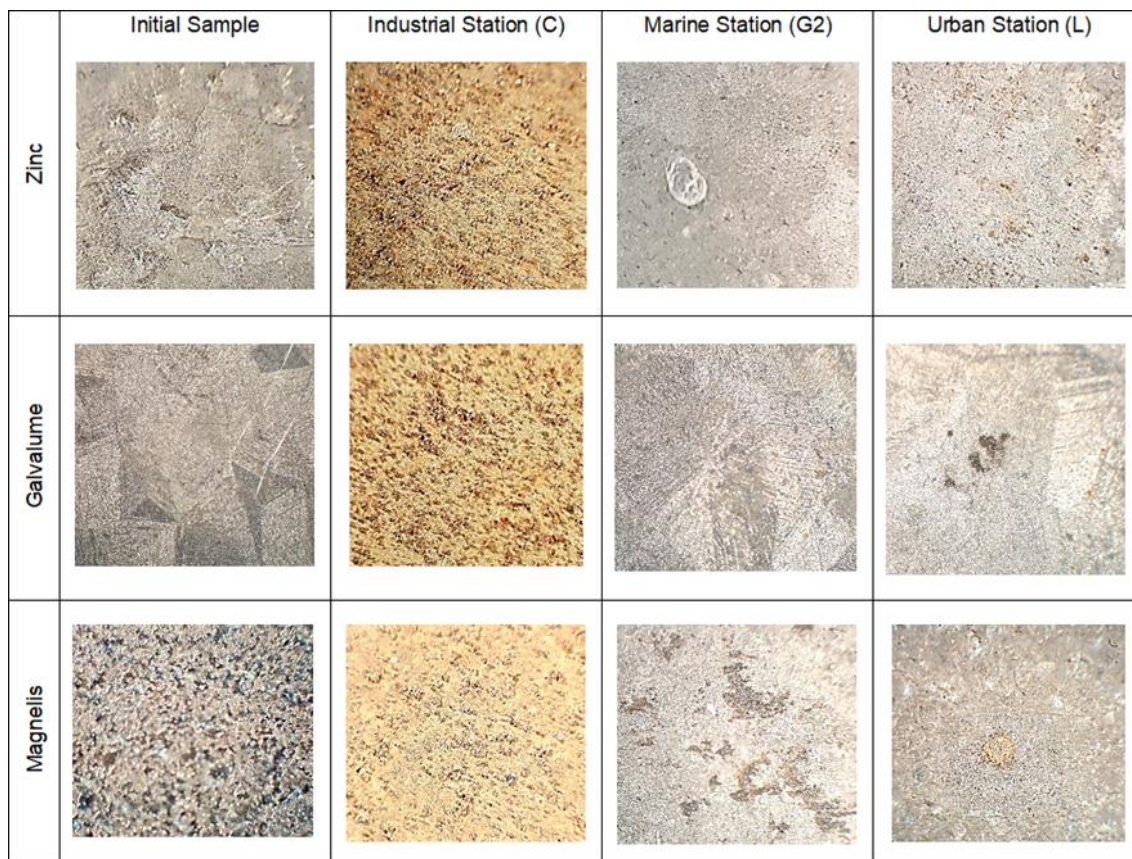


Figure 4: The degradation process of the acrylic base coating a) - Initial sample and b) - 6 Months - 9 Months - 12 Months.

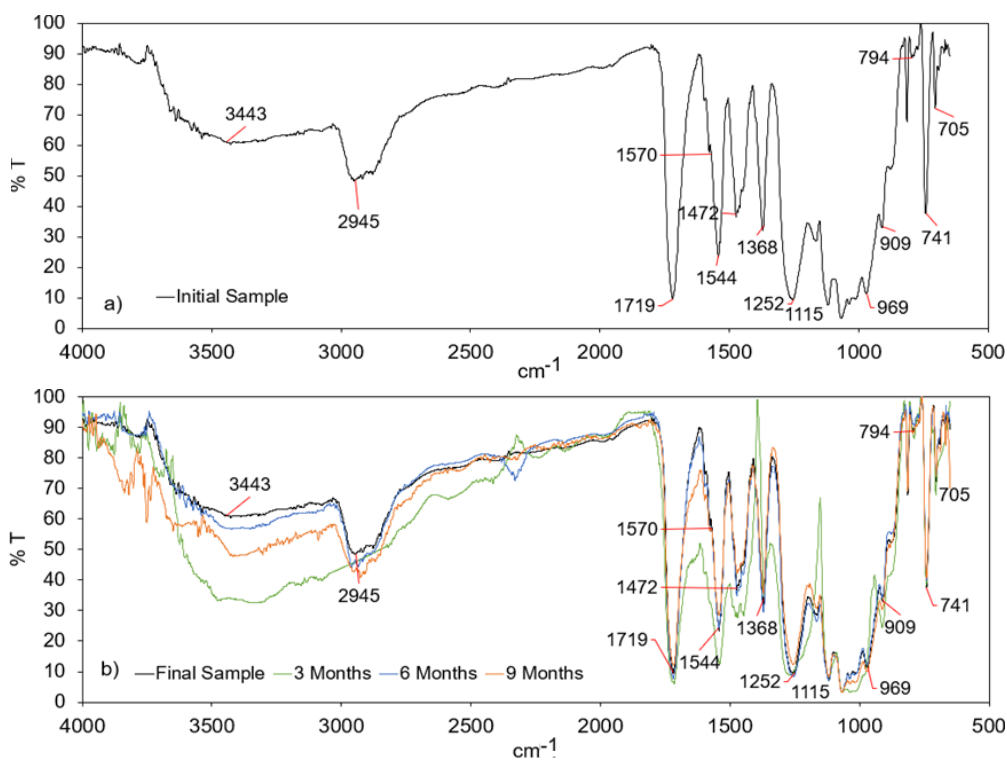


Figure 5: The degradation process of the acrylic base coating in Xenon Arc Chamber- Initial Sample - 100 Hours - 300 Hours - 500 Hours.

4. Conclusions

The corrosion behavior of carbon steel and four anticorrosive systems were analyzed in eleven different atmospheric environments in Ecuador (corresponding to nine cities). More significant corrosion in Steel occurred in the two areas. High and medium corrosivity were in the marine-industrial environment in Esmeraldas and the industrial environment of Cuenca.

Galvanized corrodes more quickly in areas with high contamination levels (such as Cuenca) and in those cities with high wetting times, such as Santo Domingo and Esmeraldas. In the stations with less SO₂ pollution and those close to the sea, thickness losses are lower. Galvalume corrodes to a greater extent in marine atmospheres (Guayaquil and Manta) than in industrial and urban atmospheres. In the case of magnelis, it is noted that there are critical losses in Esmeraldas and Cuenca. It presents a better resistance in urban environments and very humid uncontaminated environments (such as Santo Domingo). Acrylic polymeric coating shows a degree of oxidation and a slight change in color, blisters, flaking, or plastering;

also, the degree of corrosion occurred in the test stations. The highest corrosivity values were recorded in Cuenca and Esmeraldas. It is not easy to match field and laboratory tests; there are some important aspects to highlight in any case. The test under the ASTM G85 standard, given its cyclical characteristics, can better represent the atmospheric corrosive phenomenon. The Galvalume corrodes more in the test of the ASTM B117 standard due to the more fabulous presence of chlorides. The good atmospheric resistance of galvanized in marine environments is not evidenced in examining the ASTM B117 standard. It is explained due to the continuous nature of the test; protective oxides cannot be formed.

Acknowledgments

The authors would like to express their gratitude to Escuela Politécnica Nacional for the funding granted to carry out the Junior Project 17-02 "Development of high-performance polymeric coatings to protect materials subjected to aggressive atmospheric conditions in Ecuador."

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How to cite this article:

F. X. Cadena, J. E. Sosa, Resistance of Anticorrosive Coatings on Carbon Steel in Nine Cities of Ecuador. *Prog. Color Colorants Coat.*, 15 (2022), 213-223.

