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Influence of the Zinc Chromate coating on the corrosion of ASTM A-500 and galvanized A-500 steel exposed into a salt fog corrosion chamber

Influencia del recubrimiento de cromato de zinc en la corrosión de los aceros ASTM A-500 y A-500 galvanizado expuestos en una cámara de niebla salina

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Abstract

In this research work it has been analyzed the influence of the Zinc chromate coating on the corrosion of ASTM A-500 and galvanized A-500 steels exposed in a salt spray corrosion chamber, according to the ASTM B117 Standard. Two surface cleaning methods were used prior to applying the coating, considering the SSPC-SP-3 and SSP-SP-5 standards, namely a mechanical cleaning and a blast cleaning. The samples were put into the chamber with exposure times of 200, 250 and 350 h. Different equipment were used for recording the information that was used to calculate the corrosion rate. Through visual assessments according to the ASTM-D610 and ASTM D-714 standards, the corrosion degree and the blistering frequency, respectively, were determined. The materials without coating and coated after the two surface cleaning methods were compared. The results obtained have demonstrated that galvanized steel exhibited a lower corrosion rate.

Keywords: ASTM-500, anticorrosive coatings, salt spray corrosion chamber

Resumen

En esta investigación se ha analizado la influencia del recubrimiento de cromato de zinc en la corrosión del acero ASTM A-500 y A-500 galvanizado expuesto en una cámara de niebla salina acorde a la norma ASTM B117. Se realizaron dos métodos de limpieza superficial antes de la aplicación del recubrimiento, según la normas SSPC-SP-3 y SSPC-SP-5, una limpieza mecánica y otra con chorro presurizado. Las probetas se introdujeron en la cámara con tiempos de exposición de 200, 250 y 350 h. Se utilizaron diferentes equipos para registrar información que fue utilizada en el cálculo de la velocidad de corrosión. Con evaluaciones visuales, utilizando las normas ASTM D-610 y ASTM D-714, se determinó el grado de corrosión de las probetas y la frecuencia de ampollas, respectivamente. Se comparó los materiales sin recubrimiento y los dos métodos de limpieza superficial. Los resultados obtenidos han demostrado que el acero galvanizado presentó una menor velocidad de corrosión.

Palabras clave: ASTM-500, recubrimientos anticorrosivos, cámara de niebla salina

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1. Introduction

The ASTM A-500 steel, as rectangular or circular tube, is commonly used in the construction industry, as well as in the automotive industry, due to its mechanical properties and ease of welding [1]. This steel may be treated with different methods according to the particular requirement, for instance, increasing its ductility by reducing its resistance. A common application of the steel is for manufacturing bodies of vehicles, automobiles and even trucks, both cargo and for public transportation. The design of the body of a public transportation vehicle should be carried out considering the worst-case scenario in a collision, where it must be reduced the severity of the accident for the passengers and the driver [2]. One of the main agents that may cause deformation and rupture failures is the corrosion, which affects the structure of the steel and, hence, its mechanical properties. The application of an anticorrosive coating may extend the useful life of a structural element. However, it should be applied correctly, or otherwise the corrosion may be accelerated by exhibiting delaminations or blisters. Corrosion generates mass loss, mainly by reducing the area of the cross section, and even a very small reduction may decrease the resistance of the material and generate a failure [3, 4].

The most commonly used anticorrosive treatment is galvanized, because the Zn provides cathodic protection to steel thus preventing damages produced by rust and, besides, it is a low-cost element. By means of an electrochemical galvanized coating, a steel improves its corrosion resistance and even its mechanical properties by slightly modifying its composition [5]. The Zn has recyclable and non-toxic properties, and this is why more than five million tons are used yearly in anticorrosive applications, generating savings around 2200 million USD in repairs or replacements of rusty elements [6].

In order to improve the corrosion resistance of a steel immersed in Zn, different elements may be added considering the appropriate content. Kania *et al.* [7] characterized the microstructure and analyzed the corrosion resistance of a Zn coating obtained in an immersion of Zn-AlNiBi. The authors used steel with low content of Si, 0.021 %, in samples of 50 × 100 × 2 mm submerged for 180 s in the solution studied, at 450 °C. The samples were placed inside a salt spray chamber (SSCC) with NaCl at 5 % at a temperature of 35 ± 2 °C and pH between 6.8 and 7.2, from 24 to 1000 h. The mass of the samples was measured every 24 h and the results indicate that this new coating is a better anticorrosive agent than pure Zn, because the presence of corrosion was reduced 30 %, having final masses of 140.34 and 108.24 g/m^2, respectively. When the coating is inspected, Bi is observed on the surface, but it is not visualized Al or Ni, and thus authors recommend using Bi as additive instead of Pb which is environmentally harmful.

Before considering a coating to be applied at large scale in the industrial sector, various experimental tests should be carried out and the most viable alternative to analyze the corrosion rate is by means of an SSCC. Vera *et al.* [8] evaluated anticorrosive coatings in steel exposed to a marine environment, comparing field tests with an accelerated corrosion. It was used A-36 steel of 100 × 100 × 3 mm subject to blast cleaning, and a Zn-rich coating and an epoxy enamel coating were applied. The tests in the sea were conducted in Chile for 24 months, and SO_2 was collected to dissolve it in Na_2CO_3 at 5 %. The loss in thickness was between 71.9 and 222.2 μm, depending on climatic conditions, and thus it was estimated a corrosion rate of 131.4 μm/year. Using an algorithm, authors determined that similar conditions in an SSCC should be implemented at 37 °C, with a humidity of 100 % and NaCl at 3.5 % during 3000 h of exposure (125 days), reducing the time to the sixth part.

The electroplating of nanocrystalline Zn in steel to improve its corrosion resistance was analyzed by Li *et al.* [6]. The experiment used a solution of NaCl at 3.5 % and the electroplating was carried out with a bath of $ZnSO_4$ with a low carbon steel, then the samples were washed and dried. By means of a scanning electron microscope (SEM), it was visualized that the rust spot reduced from 5 μm to 40 nm, and consequently the application of this coating increased corrosion resistance almost 40 times.

Stojanović *et al.* [9] evaluated the protection to corrosion of a system with two coatings in a simulated marine environment. Naval steel plates of 120 × 70 × 3 mm were subject to blast cleaning to apply two layers of anticorrosive coating, each of 150 μm, and further an anti-fouling coating. The plates were exposed for 1440 h in an SSCC at 38.08 % and a pH of 8, where two groups were selected, one for immersion and another for agitation. Results indicate that the plates that were agitated in the solution produce more microorganisms and, as a result, a greater corrosion; in addition, the second coating did not have the appropriate adherence, and thus authors recommend analyzing the chemical composition of the anticorrosive coatings

The corrosive behavior of the ASTM-SA213-T22 steel coated with Cr_2O_3 in a saline environment at 700 °C was analyzed by Goyal *et al.* [10]. The samples were of 22 × 15 × 3 mm and coated with commercial Cr_2O_3 with a thickness between 250 and 255 μm. A furnace was used to generate heat corrosion with Na_2SO_4 at 60 % for 1 h, and the final mass of the samples was considered. The base material showed a larger corrosion rate compared with the Cr_2O_3 coating that had a perfect adherence, causing that the mass of the material remained at 94.5 %.

This research is aimed at determining the influence of a zinc chromate coating in the corrosion of ASTM A-500 and galvanized A-500 steels, used for manufacturing bodies of public transportation vehicles. In this way, it will be established if it is required this prior treatment. The document is distributed as follows. The Materials and methods section describes the steps of the experimental process considering different standards for conducting it. Results presents figures and the comparative analysis of the samples after their exposure to the SSCC. At last, the Conclusions explain the results obtained and define which steel had the lowest corrosion.

2. Materials and methods

Figure 1 summarizes the procedure considered for the experimental development, and for obtaining the results of this research.

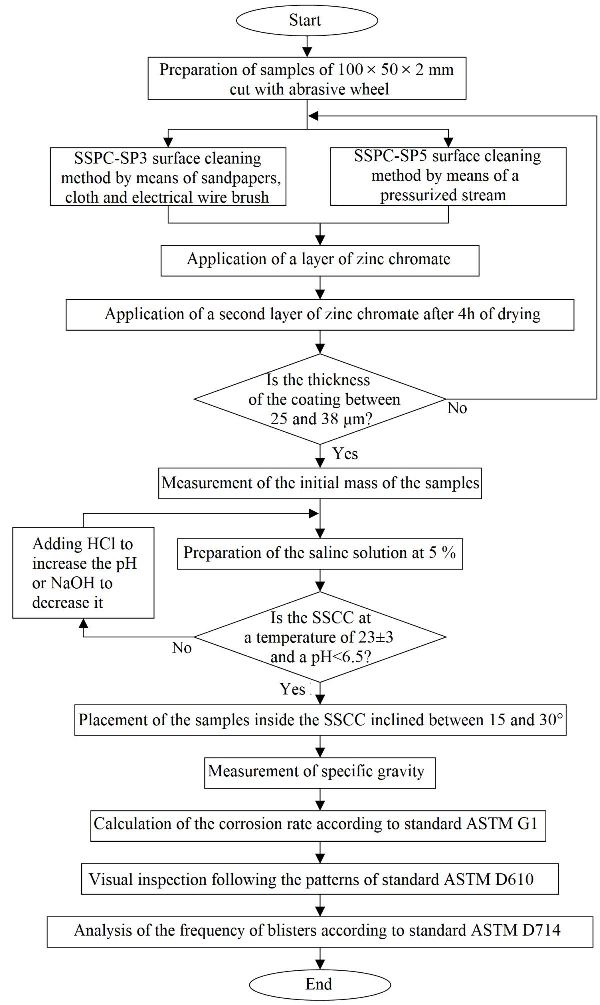


Figure 1. Flow diagram for the experimental development

2.1. Preparation of the material

The material used was a tube of ASTM A-500 carbon steel obtained by means of cold seamless welding, used for manufacturing vehicle bodies. Using a matrix of experimental design, it was established that it is required eight samples of each material, and for such purpose, they were cut by means of an abrasive wheel using a grinder, thus getting plates of 100 × 50 × 2 mm.

2.2. Surface cleaning

The Society for Protective Coatings (SSPC) has regulated specific surface cleaning procedures required before applying an anticorrosive coating. Two surface cleaning methods have been chosen for this research, the first corresponds to a mechanical cleaning, according to standard SSPC-SP-3 [11], using sandpaper to remove rust layers. Afterwards, it is required a rotating wire brush as electrical tool to clean the surface and remove all debris. It is important to mention that, due to the geometry of both the material and tools, it is possible that there may remain debris hidden in the irregularities of the material.

The standard SSPC-SP-5 [12] was considered for the second surface cleaning method, which consists of using a pressurized liquid to remove all particles on the surface of the material. This method assures a total cleaning, free of delaminations, since a pressurized stream enables removing even dust and grease, such achieving a better adherence of the coating.

2.3. Coating

A zinc chromate coating was applied on the eight samples of A-500 and galvanized steel, four to be cleaned with SSPC-SP-3 and the remaining four with SSPC-SP-5. This coating consists of resins and pigments that provide corrosion resistance in the presence of different atmospheric agents; in addition, it is one of the most widely used commercially.

The coating was diluted in thinner in a 4 to 1 proportion for its application using a blowtorch. According to the manufacturer, the thickness of the coating must be between 25 and 38 μm, and thus two layers were applied with a drying time between them of 4 h at 20 °C. The Elecometer 456 was used for measuring the thickness of the coating.

2.4. Test in the SSCC

The ASTM B-117 standard [13] was used for the experimentation in the SSCC, which indicates preparation, procedures, prediction and results under a controlled corrosive environment. It was used a saline solution at 5 %, with 12.72 kg of NaCl in a volume of 240 liters of distilled water.

Among the measuring instruments that were used, it is important to mention the HANNA HI9125 waterproof pH meter, to verify that the pH is less than 6.5 at an average temperature of 23 °C. If the pH value decreases, NaOH may be added, otherwise, when the pH is high, HCl is added until obtaining the required value. By means of a flow meter, 2 ml/h of NaCl were collected from the SSCC every 24 hours. An MA887 digital salinity refractometer was used as a salinity meter to determine the specific gravity of NaCl. The mass of the samples, of the base material and of the material with the coating, was measured before entering them in the SSCC, where they were placed at an inclination of 20 to 30º.

For the zinc chromate coating, the average time for the test was estimated in 250 h. Different exposure times inside the SSCC were established, having 200, 250 and 350 h to determine how this exposure time influences steel corrosion. After each period, the weight of the samples was measured again to calculate the mass loss between the initial and the final values.

2.5. Corrosion rate

According to the ASTM G-1 [14] standard, this parameter is defined as the thickness loss of a steel per unit time to analyze the damage produced by corrosion after the exposure. The corrosion rate ($\dot{C}$) is a function of the material, as well as of the exposure time, and may be obtained as:

$$\dot{C} = (K \cdot W) \cdot (A \cdot t \cdot \delta)^{-1} \tag{1}$$

Where K remains constant at a value of 8.76×10^4 mm/year, W is the mass loss expressed in g, A is the area of the sample in cm^2, t are the exposure hours and δ if the steel density in g/cm3.

2.6. Visual evaluation

The ASTM D-610 standard [15] was considered for evaluating the corrosion degree on a coated surface, to determine if the coating shall be repaired or replaced. According to this standard, a scale from 1 to 10 has been established as a function of the surface area of corrosion, where 10 is used to indicate rust stains which are 0.01 % smaller than the total area, while if the corroded area is larger than 33 %, it is assigned a value of 1. This number should come along with a letter to indicate the corrosion visual pattern, stained (S), punctuated (P) or general (G).

This visual evaluation is reinforced with a second inspection, which consists of evaluating the blisters produced by corrosion on the coating according to the ASTM D-714 standard [16]. A number between 0 and 10 has been assigned for identifying blisters, where 10 corresponds to a surface without imperfections, 8 indicates small blisters which are difficult to detect with the naked eye and the smaller numbers indicate increasingly bigger blisters. In addition, this number comes along with a letter that represents the frequency of presence of blisters per unit area, indicating if this frequency is few (F), medium (M), medium dense (MD) or dense (D).

3. Results and discussion

3.1. Corrosion rate

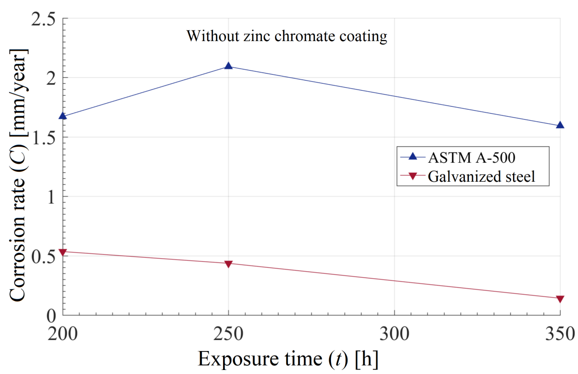
When considering the difference between the initial and final mass of the samples, it was possible to calculate the corrosion per year. In the following, values of corrosion rate obtained with Equation (1) are presented for the base material and for the samples with the SSPC-SP-3 and SSPC-SP-5 surface cleaning methods.

The samples of ASTM A-500 steel and of galvanized steel without the zinc chromate coating exhibited a corrosion rate of 1.672 and 0.535 mm/year after 200 h of exposure in the SSCC, as shown in Figure 2a. On the other hand, with the SSPC-SP-3 mechanical cleaning, the values were 0.129 and 0.044 mm/year for the A-500 and galvanized steel, respectively, for the same exposure time. At last, for the A-500 and galvanized steel samples that were subject to blast cleaning according to the SSPC-SP-5 standard, corrosion rates of 0.051 and 0.034 mm/year were obtained. The values of corrosion rate tend to grow as the exposure time increases, however, the rust on the surface of the samples may create an additional coating and this value may decrease.

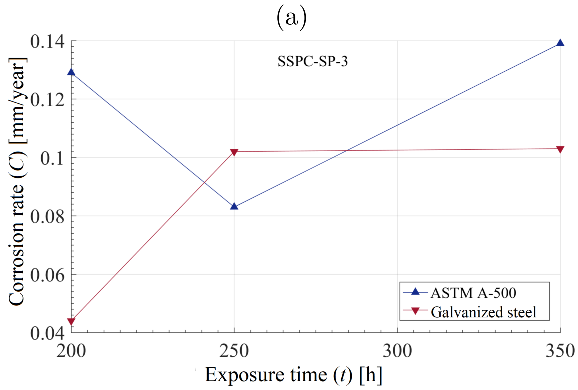
After 250 h of exposure, the A-500 samples with the surface cleaning methods and zinc chromate coating decreased the value of corrosion rate, yielding 0.083 and 0.014 mm/year for methods SP-3 and SP-5, respectively, while the base material increased its corrosion to 2.092 mm/year. With the same exposure time, the galvanized steel showed opposite results, where the base material decreased its corrosion to 0.436 mm/year and the SP-3 and SP-5 methods increased in 0.058 and 0.002 mm/year, respectively, with respect to an exposure of 200 h.

At last, with an exposure time of 350 h, the base material samples of A-500 and galvanized steel had a corrosion of 1.594 and 0.142 mm/year. For the SSPC-SP-3 surface cleaning, these steels showed a corrosion rate of 0.139 and 0.103 mm/year, respectively. In addition, with the SP-5 surface cleaning method, the samples recorded values of 0.033 and 0.029 mm/year for the A-500 and galvanized steel, respectively.

The values obtained are more closely grouped for the SSPC-SP-5 cleaning, having a standard deviation of 0.0185 and 0.0036 mm/year for the A-500 and the galvanized steel, respectively. These steels had a standard deviation for the SSPC-SP-3 method of 0.0299 and 0.03378 mm/year, respectively, and besides, 0.2679 and 0.2044 mm/year without treatment.



(a)



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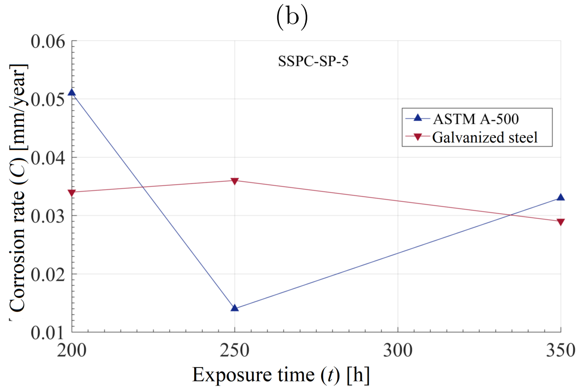
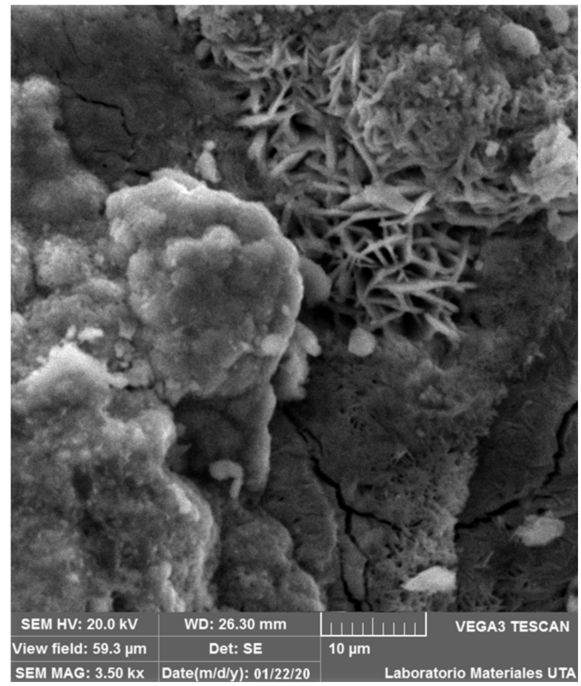


(c)

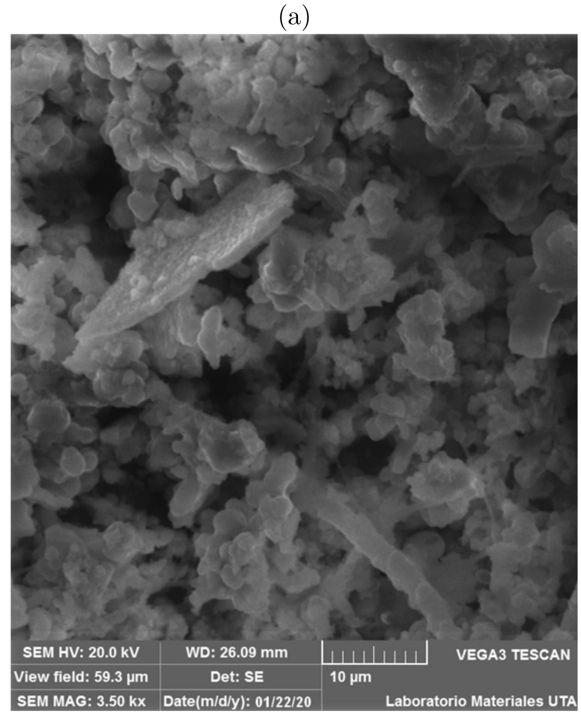
Figure 2. Corrosion rate for samples a) without coating, b) SSPC-SP-3 cleaning, c) SSPC-SP-5 cleaning

3.2. Visual evaluation

By means of an SEM microscope, it was visualized the morphology of the corrosion products in the A-500 samples. Figure 3a shows a sample without coating exposed for 300 h, where it is observed a formation generated by corrosion which is known as lepidocrocite. Figure 3b presents the analysis of the morphology of the sample with an exposure time of 350 h, where it is identified semicrystalline goethite shaped like clouds, as well as very thin sheets of lepidocrocite, with a contour similar to roots.



(a)



(b)

Figure 3. Microstructure of the ASTM A-500 steel without coating exposed in the SSCC a) 300 h, b) 350 h.

Figure 4a indicates the results of the corrosion existing in the ASTM A-500, while Figure 4b shows the corroded galvanized steel, after 200, 250 and 350 h of exposure in the SSCC. The samples appear as surfaces with a lot of corrosion, visible to the naked eye, and even with significant accumulations, verifying the calculated values of corrosion rate.

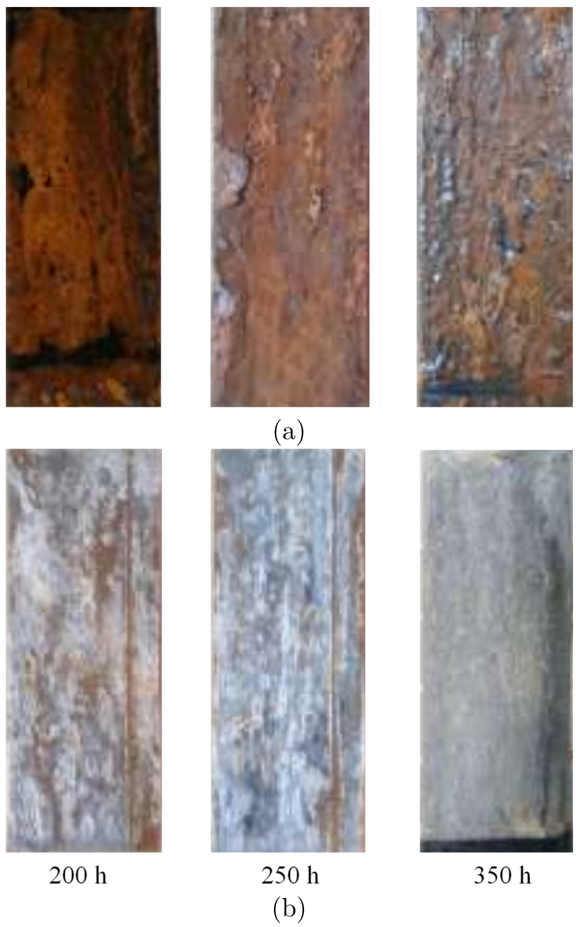


Figure 4. Samples of base material exposed to the SSCC a) ASTM A-500, b) galvanized steel

The patterns of the ASTM D-610 standard were used as reference to perform an evaluation of the percentage of surface corroded. In addition, this visual evaluation was complemented indicating the frequency and size of the blisters present in the samples according to the D-714 standard.

Figure 5a shows the coated A-500 samples with SSPC-SP-3 surface cleaning, where corrosion stains in about 3 % have been indicated corresponding to 5 S after 200 h. For the sample exposed for 250 h, a corrosion of 5 G has been considered and the sample that was in the SSCC for 250 h was evaluated as 3 G.

The frequency of the blisters was measured for the samples with exposure time of 200 and 350 h, indicating an evaluation of 6 M and 2 M, respectively. On the other hand, for the sample exposed for 250 h this frequency was larger, assigning it a value of 6 MD with visible blisters.

The ASTM A-500 samples with SSPC-SP-5 cleaning prior to the application of the zinc chromate, are indicated in Figure 5b, after exposure times of 200, 250 and 350 h, respectively. For the sample that was exposed for 200 h, it was assigned a corrosion of 4 G, while the samples with exposure time of 250 and 350 h, were evaluated as 5 G.

None of the samples evidenced the existence of blisters, indicating that the coating had a good adherence.

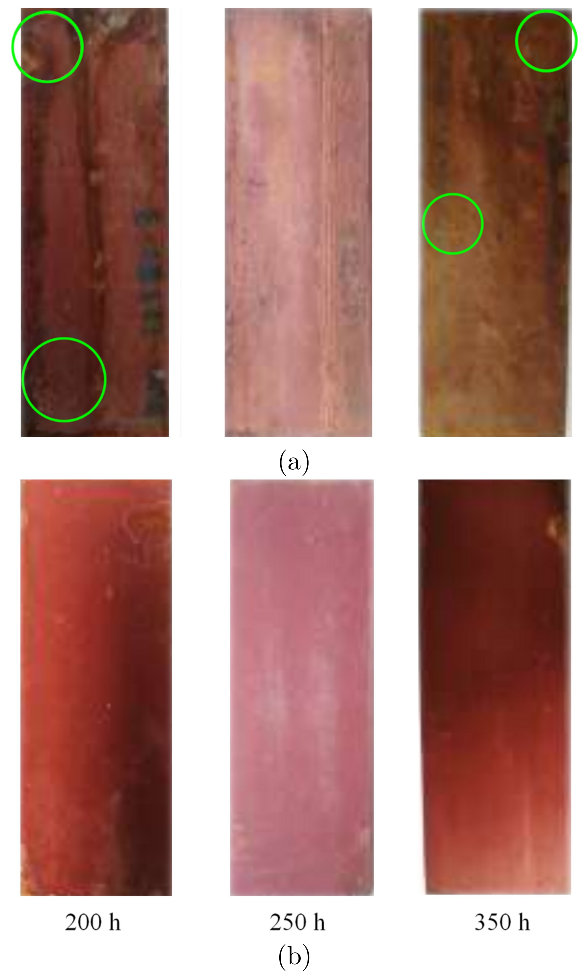


Figure 5. ASTM A-500 samples exposed to 200, 250 and 350 h, a) SSPC-SP-3, b) SSPC-SP-5

Figure 6a presents the galvanized steel samples cleaned with the SSPC-SP-3 method and coated with zinc chromate. In the sample that was in the SSCC for 200 h, there was evidence of corrosion stains, yielding 5 S and there were no blisters on its surface. For the sample exposed for 250 h, a general corrosion is visible, yielding 6 G and small blisters were visualized, thus assigning it a 6 M. Regarding the sample with exposure time of 350 h, a corrosion of 4 S has been assigned due to visible stains, and it had 6 F because the frequency of blisters is low, although such blisters are significant. The galvanized steel samples with SSPC-SP-5 cleaning are shown in Figure 6b.

In the galvanized steel sample with exposure time of 250 h it was not possible to visualize signals of corrosion and there are small blisters, having a frequency of 8 M. Regarding the samples exposed for 200 and

350 h, they show small corrosion stains, thus they have been assigned 5 S and none of them has shown blisters on its surface.

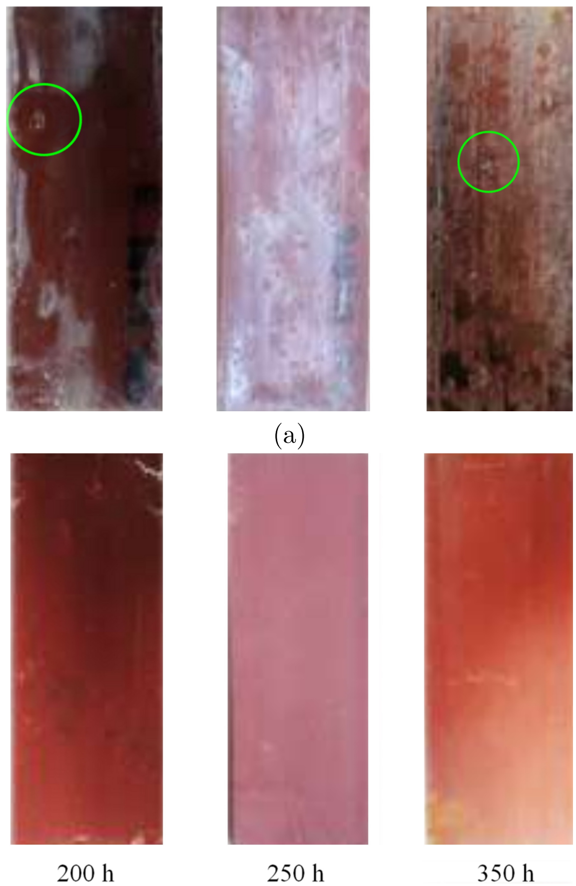


Figure 6. Samples of galvanized ASTM A-500 exposed for 200, 250 and 350 h, a) SSPC-SP-3, b) SSPC-SP-5

4. Conclusions

The values obtained of corrosion rate for the samples indicate that the corrosion affects more during the initials hours of exposure. For the A-500 steel after 200 and 250 h of exposure, there was a corrosion rate of 1.672 and 1.594 mm/year, respectively. For the galvanized steel without coating, the values obtained were 0.535 and 0.142 mm/year for similar times. This trend remained during the tests with samples cleaned using SSPC-SP3 and SSPC-SP5 for both materials.

The A-500 steel without treatment had a maximum corrosion rate of 2.092 mm/year, in the sample exposed for 250 h in the SSCC, which is 3.9 times higher than the largest value reached for the galvanized steel. With the SSPC-SP-3 method, the A-500 steel and the galvanized steel reached a maximum of 0.139 and 0.103 mm/year, for a difference of 25.9 %. With the cleaning according to the SSPC-SP-5 standard, the highest corrosion rate was 0.051 and 0.036 mm/year for the A-500 and the galvanized steel, respectively. Then, in the steels without coating it is evident that the galvanized is an anticorrosive protection, although it continues exhibiting higher values than with coating. The corrosion may be considered similar for both materials, but the SSPC-SP-5 methods yields lower corrosion in the samples.

When considering the analysis between the two surface cleaning methods, according to the ASTM D-610 standard, it was obtained that the A-500 and the galvanized steel cleaned with the SSPC-SP-3 method exhibited a general surface corrosion and stained between 5 S and 5 G to 6 G. This evaluation was reduced in the samples treated with the SSPC-SP-5 cleaning, considering the samples with a general 4 G corrosion.

The ASTM D-714 standard was used for complementing the visual evaluation and determining the frequency and size of the blisters. In the A-500 and galvanized steel samples cleaned according to the SSPC-SP-3 standard, maximum and minimum evaluations of 2 M, 6 MD and 6 M, 6 S, respectively, were obtained. Therefore, it may be stated that the zinc chromate coating adheres similarly in both materials and provides an anticorrosive protection 7.7 and 8.2 times higher compared to the A-500 and galvanized steel without coating, respectively.

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