The effect of zinc thickness on corrosion film breakdown of Colombian galvanized steel

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Abstract. This work studies the corrosion behaviour of Colombian galvanized steel in solutions of chloride and sulphate ions. The effect of the thickness and exposure time on the film’s breakdown susceptibility and protectiveness of the corrosion products were studied using potentiodynamic polarization curves and electrochemical impedance spectroscopy. The corrosion products were analysed using SEM-EDS and XRD. The samples with a higher thickness level in the zinc film (Z180) have the lowest corrosion rate. In this case, one of the products that was formed by the chemical reactions that occurred was Zinc hydroxide, which exhibits a passive behaviour as observed in the Pourbaix curves of the obtained potentials and in how the different Ph levels of the solutions worked. The sheets with the highest thickness (Z180) had the best performance, since at the end of the study they showed the least amount of damage on the surface of the zinc layer. This is because the thickness of the zinc layer favours the formation of Simonkolleite, which is the corrosion product that protects the material under the conditions of the study.

1. Introduction

The search for steel with corrosion resistance optimized for use in the construction, the automotive and the manufacture of household appliances industry has motivated numerous research work [1-7]. In this sense, galvanized steels have played a very important role in the improvement of the corrosion resistance of steels used in these areas [8-11]. These steels with zinc-based coatings act as a barrier layer and as cathodic protection. The effect of the barrier layer is produced by the insulation of the steel from the environment through two different layers formed during the different stages of the corrosion process. The first barrier is the zinc coating itself, which is progressively replaced in its insulation function by the formation of a zinc corrosion products layer. Cathodic protection means that even if the steel substrate is exposed, the zinc layer will still corrode [12-14]. The zinc-based coating can be obtained by electrodeposition, thermal spraying or immersion in liquid metal baths (hot dip) at 450°C [5-16]. The most industrially popular zinc coatings in Colombia are the galvanized ones (Zn-0.2% p/p de Al) [2].

Recently, Ramirez et. al. [1] discovered that the size of the zinc crystal is a determinant factor in the corrosion resistance of this material; according to their results a smaller size of the zinc crystal favours the corrosion resistance of the sheet of galvanized Steel. On the other hand, Sandoval et al. [2] have found that the corrosion potential and the corrosion rates of the galvanized steel sheets increase
with the immersion time and observed chopped corrosion in sheets that were studied after 30 days of immersion.

For that reason, the effect of galvanizing the thickness and the exposure time on a solution with chlorides and sulphates on the corrosion resistance of a galvanized steel in Colombia, was evaluated using potentiodynamic polarization curves and electrochemical impedance spectroscopy.

2. Methodology

In order to evaluate the breakdown of the protective layer of galvanized Steel in this study, the following variables were taken into account: time (0, 7 and 14 days of exposure), thickness of the galvanized layer (90, 120, and 180g/m² of Zinc) and effect of Cl⁻ ion (15.15g/L NaCl) y SO₄²⁻ (16.08g/L Na₂SO₄). The samples used in this work were named Z90, Z120 and Z180, these names were given considering the thickness of the galvanized layer. Two sample groups were cut, the first group’s dimensions were 2.0cm×2.0cm. These samples were used to conduct a saline exposure test and to characterize the corrosion products formed after 14 days of immersion. The second group of samples was cut with dimensions of 6.0cm×10.0cm. These were used to carry out the electrochemical tests on the galvanized Steel. In both cases, the area of exposure of the samples was 1cm². For the electrochemical characterization, a flat three–electrode cell was used (see Figure 1) and the open circuit potential was recorded for 1 hour before each electrochemical test. The electrochemical impedance spectroscopy was obtained by applying 10mV AC, performing a frequency sweep of 0.01 to 100000Hz and recording 10 points per decade. Potentiodynamic polarization curves were performed within a potential range of −500mV to 2000mV, with a scanning speed of 1mV/s. Finally, the morphology of galvanized Steel sheets and corrosion products was observed by Scanning Electron Microscopy (SEM); the elemental composition of the corrosion products was identified by EDS and the crystalline phases were identified by XRD.

3. Results and analysis

Figure 2 shows the Nyquist diagrams obtained under the study conditions and the equivalent circuit models used to make the impedance spectra adjustments. In Figure 2(a), an inductive lasso is show in sheet Z90, which is associated with the adsorption of species on the surface. These species generally result in the formation of corrosion products on the surface of the galvanized Steel and they can be the reason for the good performance shown by this sheet in the initial test. Figure 2(b) shows the effect of the sulphate and chloride ions, it can be observed that the sulphate ion causes the greatest deterioration of the galvanized sheets. This happens because this ion forms compounds that are soluble in the solution and are reabsorbed by the surface continuously. The intermediate behaviour that can be observed in sheet Z120 is due to the fact that the corrosion products created by sulphate protect the surface of the sheet, but since they are corrosion products with a porous morphology, these allow the passage of chloride ions, which cause the breakdown of the galvanized Steel sheet Z180. This is due to the thickness of the galvanization and to the formation of passivating layers on its surface.
Figure 2. Nyquist diagrams of galvanized steel exposed at different times, (a) 0 days, (b) 7 days, (c) 14 days, (d) and (e) Equivalent circuits used to adjust EIS data.

Figure 2(e) shows the equivalent circuit with which the impedance spectrum exposed sheet Z120 was adjusted for 14 days, while the circuit of Figure 2(d) was used to adjust the other spectra. Table 1 shows the parameters of the equivalent circuits. The parameter Rp refers to the polarization resistance in different sheets and this was determined by the sum of contributions made by the resistance of the galvanized layer and interface metal coating. It can be observed that the Z180 galvanized Steel sheet was the one with the highest Rp after the 15 days of immersion. This high value in the parameter Rp is associated with a good corrosion resistance.

Table 1. Polarization resistance obtained from the adjustment to equivalent circuits of the EIS data.

| Sample | 0 days | 7 days | 14 days |
|--------|--------|--------|--------|
|        | Z90    | Z120   | Z180   | Z90 | Z120 | NaCl | Z120 | Na2SO4 | Z180 | Z90 | Z120 | Z180 |
| Rp (kΩ/cm²) | 205 | 52.7 | 5.62 | 1.01 | 1.81 | 0.35 | 7.4 | 1.47 | 0.47 | 3.54 |

Figure 3 shows a very low slope at the beginning of the anode zone, which is associated with a rapid increase in current. This suggests that the anode processes are present in the cathodic zone since the reactions are associated to processes controlled by concentration. This happens because zinc tends to form corrosion products spontaneously on its surface under the study conditions. On the other hand, it can be seen that the Cl⁻ and SO₄²⁻ ions acting separately can generate shifts in the corrosion potential towards more positive values. In addition, the presence of the sulfate ion is able to decrease the density...
of the passivation current, which is attributed to the formation of corrosion products that protect the sheet of galvanized steel.

Figure 3. Potentiodynamic polarization of galvanized steel at 7 days.

In Figure 4, it can be observed that after 15 days of exposure, corrosion with red colour products formed on the Z90 sheet and white corrosion, which shows that a total breakdown of the galvanizing layer has been achieved, was also formed. The white corrosion is attributed to the formation of oxide compounds and the precipitation of salt that protects the material from corrosion. Additionally, it can be observed that as the exposure time increases, the corrosion rate is higher except for the sheet Z180 at 14 days, where there is a decrease in the corrosion rate attributed to the formation of simonkolleite as shown in EDS and DRX results.

Figure 4. Corrosion rates of galvanized steel sheets at different exposure times.

The elemental composition maps of Figure 5 show that in the Z90 sheet there are dark areas in the zinc map that corroborate that the zinc layer has been destroyed. Images corresponding to sheet Z120 show the formation of a salt agglomerate which can be observed on the surface, where zinc is displaced by oxygen, sulphur, chlorine and sodium. This indicates that the zinc layer has been destroyed and corrosion products have been formed. On the other hand, it is possible to observe the
formation of a homogeneous layer of salt on the surface, which is a characteristic of white corrosion. It is also possible to observe that the distribution of zinc on the surface is uniform and that the base material has not been attacked yet. Through the XRD analysis, it was found that corrosion products formed on the galvanized Steel sheet Z90 (Gordait, Zinc and sodium hydroxide) and Z120 (Gordait, Zincite, Sodium Chlorate and Ammonium Sulphate) are corrosion products that demonstrate the attack and deterioration of the protective zinc layer. The products formed on sheet Z180 (simonkolleite, zincite, zinc hydrogen sulphate, halite, sodium, chlorate, sodium sulphate and gordaita) showed that sheet Z180 had the best performance against corrosion and less damage in the galvanized layer, which is mainly attributed to the thickness of the layer and to the formation of simonkolleite on the surface of the sheet.

![Figure 5. Chemical composition maps of exposed galvanized steel at 14 days exposure.](image)

4. Conclusions
The exposure time of samples to chlorides and sulphates and grain size are factors that negatively affect the corrosion behaviour of galvanized Steel sheets. The thickness of the galvanization improves the corrosion properties of galvanized steel sheets, therefore, the penetration of chloride ions into the substrate will be more difficult. Although the Z90 sheet had the best performance against corrosion due to its small grain size, its coating was completely corroded with red corrosion on its surface, which is a characteristic of the iron oxides, indicating that the substrate was corroded.

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