

Corrosion Performance of Conversion Treatments for Electrogalvanised Steel Sheet

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Abstract

Chromate conversion treatments have been widely used due to their excellent corrosion resistance properties; however, their use is increasingly restricted because of the highly toxic chromic acid solutions required, with consequent effluent disposal and ecological problems. The removal of these toxic chemicals is considered a priority within most of the developed countries. In this work, the corrosion resistance of different alternative pretreatments applied on electrogalvanised steel sheet: 1) Cr(III) and Zr complexes layer, 2) Ce(III) layer, 3) Ce(III)/Ce(IV) double layer, 4) Cr(VI) chromating was investigated, and its results compared with those from the tests performed using bare electrogalvanized steel sheets as a substrate. These samples were exposed to aerated 0.05 mol/L NaCl or 0.1 mol/L Na₂SO₄ solutions. The electrochemical behavior of samples was studied by electrochemical techniques. For three days of immersion in the solution test, the experimental results have shown that, compared with the Cr(VI) protective properties, the Cr(III) + Zr complex layer presented similar performance. Even though the initial corrosion resistance was offered by the Ce(III) and Ce(VI)/Ce(III) conversion coatings was relatively good, it quickly decreased as a function of the exposure time.

Keywords

Pre-Treatments, Conversion Coatings, Corrosion, EIS, Electrogalvanised Steel

1. Introduction

The corrosion of electrogalvanised steel is one of the major problems in industry. The material could become more resistant to corrosion if a protective con-

version coating is applied on top of the zinc layer. The term “conversion coating”, as used in the metal-finishing industry, refers to the conversion of a metal surface into a surface that will more easily accept applied coatings and/or provide a more corrosion resistant surface [1]. Conversion coatings for zinc have been in use since the early 1920's and there are several different products on the market [2]-[16]. These layers protect the zinc coating by acting as a physical barrier to the inducing corrosion species (water, oxygen and ions), and corrosion inhibitor. Furthermore, when the surface is scratched or mechanically damaged, enough water is absorbed by the layer to swell and mend the damaged areas (self-healing effect) [17].

The Cr(III)-based conversion coating technology was commercially introduced in the late 1980's as an earlier attempt to replace the carcinogenic hexavalent chrome from as many metal-finishing processes as possible [18]-[32]. Tomachuk *et al.* [33] evaluated the corrosion behavior in zinc coatings obtained from a cyanide-free alkaline bath, then subjected to Cr(III)-based passivation treatments with or without sealing treatment and submerged in different electrolytes. The experimental data analysis allowed to infer that the Cr(III)-based conversion treatment with a suitable sealant provides good corrosion resistance. Also, that still performs better attached to a suitable painting system due to an increased amount of white corrosion products covering the surface micro-defects act as a barrier to oxygen and ionic species diffusion through the conversion layer. Furthermore, the Cr(III) layer also decreased the rate of the oxygen reduction reaction during oxidation of the zinc substrate.

As well, among the chromate-free and environmentally friendly pre-treatments developed so far, the application of Zr-based conversion coatings has gained acceptance [34] [35] [36] [37]. They are currently introduced in several industrial applications, such as in the automotive industry. Puomi *et al.* [38] showed that the Zr-based conversion coatings on galvanized steel and Galfan steel is mainly composed of ZrO_2 and their thickness < 50 nm. The ZrO_2 has very attractive properties, such as improved resistance to wear and corrosion, heat resistance and good adhesion to metallic surfaces [39]-[50].

Hinton *et al.* made the first research on the rare earths salt-based treatments [9] [10] [51]. They found that cerium was effective in reducing the corrosion cathodic reaction. Other authors also investigated the mechanism of corrosion inhibition on zinc treated with Ce salts [52]-[58]. Aramaki [59] proposed modifying the Ce_2O_3 film usually formed on the treated surface, oxidizing with H_2O_2 . The result was the formation of a highly resistant layer to the 0.5 mol/L NaCl solution. XPS (X-ray photoelectron spectroscopy) analysis showed the formation of a thin film (thickness < 50 nm) containing a small amount of Ce(IV) which is derived from the oxidation of Ce(III) by the H_2O_2 . The coexistence of Ce(IV) is still investigated [60]. Shibli [61], developed a nanoparticulate CeO_2 film where in $Ce(NO_3)_3 \cdot 6H_2O$ was incorporated into the zinc bath. The coating produced had a thickness of 50 μm ; however the thickness of the CeO_2 film was approximately 20 nm to 40 nm. Hamlaoui [62] investigated the electrodeposition of

layers obtained from electrolytes based on cerium salts on galvanized steel. He found that the more concentrated solution to lower its pH and, therefore, working in highest concentration was vigorous bubbling confirming the presence of large amounts of $H_2 \uparrow$. However, if the film was treated with cerium PEG (polyethylene glycol) after passivation, this reduced the number of cracks in the deposit by reducing the hydrogen present in the aqueous medium or by decreasing the film thickness. Montemor *et al.* [63] and Ferreira *et al.* [64] have studied the effect of treatment time on the chemical composition and corrosion behavior of $Ce(NO_3)_3$ conversion coatings for galvanized steel and found that the film composition and thickness change with time.

As an extensive research is still needed to find effective but non-toxic and environmentally friendly conversion treatments for replacing the based on Cr(VI), the aim of the present work was to study the protective performance of: 1) Cr(III) + Zr complex layer; 2) Ce(III) layer; 3) Ce(IV)/Ce(III) double layer; or 4) Cr(VI) chromating (as reference) applied on electrogalvanised steel sheets. For this, replicates of the coated sheets were immersed for 72 h in aerated 0.05 mol/L NaCl or 0.1 mol/L Na_2SO_4 solutions and their behavior investigated through AC (electrochemical impedance spectroscopy-EIS) and DC (potentiodynamic polarization) electrochemical techniques. The EIS data were fitted and interpreted by means of equivalent electrical circuit models.

2. Experimental Details

2.1. Preparation of Electrogalvanised and Passivated Samples

1) Panels of low-carbon steel (AISI 1010) with dimension of 7 cm × 10 cm and 0.1 cm thickness were degreased in an alkaline solution (based on KOH, triethanolamine and K_2SiO_3) at $22^\circ C \pm 2^\circ C$, and polarization with a current density of 4 A/dm² for 3 min. Then, these panels were rinsed in deionized water, subjected to pickling in HCl 1:1 with an iron inhibitor for 1 min, newly rinsed with deionized water, activated in 5% wt ammonium bifluoride solution for 30 s, and rinsed once more in deionized water. Once this step was completed, the steel samples were electrogalvanised using a cyanide-free alkaline bath containing Zn^{2+} 12.5 g/L, KOH 170 g/L, K_2CO_3 50 g/L, leveler additive 10 mL/L, brightening agents 1 mL/L, conditioner 10 mL/L. The cathodic current density was 2 A/dm² operated at $22^\circ C \pm 2^\circ C$ for 45 min [32]; these samples were identified with the symbol (Z).

Immediately after applying the electrogalvanising step, the surface was activated in 0.5% v/v HNO_3 solution, pH = 1, for 10 s, rinsed in deionized water, and pretreated with any of the conversion products specified as follows:

2) Blue-colored Cr(III)-Zr(IV)-based conversion treatment (symbol ZCrZr) whose operating parameters were pH = 4.2 (adjusted with 1% v/v NaOH or 5% v/v H_2SO_4 solutions), immersion in the industrial bath for 30 s, temperature $22^\circ C \pm 2^\circ C$, and mechanical stirring. The passivation bath was composed by hexafluoro silicic acid + trivalent chromium ions + zirconium complexes (com-

mercial product).

3) Pale iridescent colored Ce(III)-based conversion treatment (symbol ZCe) whose operating parameters were pH 3.5, immersion for 30 s, temperature $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$, and mechanical stirring. The passivation bath was composed by 2.5 g/L $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, 1 mL/L H_2O_2 , and 0.1 g/L H_3BO_3 . The pH = 3.5 (adjusted to with 1%v/v NaOH or 5% v/v H_2SO_4 solutions).

4) Pale iridescent colored Ce(IV)/Ce(III) bilayer (symbol ZCeD). The first layer was obtained in 1 g/L $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ solution, and the second one in 2.5 g/L CeCl_3 , 1 mL/L H_2O_2 , and 0.1 g/L H_3BO_3 . The operating parameters in both passivation baths were pH = 3.5 (adjusted with 1% NaOH or 5% H_2SO_4 solutions), immersion for 30 s, temperature $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$, and mechanical stirring.

5) Yellow-colored Cr(VI)-based conversion treatment (symbol ZCr6) used as reference samples. The operating parameters were pH = 1.8, immersion for 30 s, temperature $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$, and mechanical stirring. The passivation bath was composed by 4.6 g/L $\text{Na}_2\text{Cr}_2\text{O}_7$, conductive salt (NaCl), and diluted HCl for pH adjustment.

At finishing the conversion treatments, the samples were rinsed in deionized water and dried for 15 min at 80°C . All the samples were stored in desiccators at $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$ up to their use.

2.2. Thickness Measurements

Coatings thickness was measured using the X-Ray Fluorescence Method, Helmut Fischer mod XDL-B according to the ASTM B568-98 standard [65].

2.3. Electrochemical and Corrosion Behavior

The corrosion resistance of the conversion coatings was evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy in aerated 0.05 mol/L NaCl or 0.1 mol/L Na_2SO_4 solutions at $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

The electrochemical cell consisted of a classic three-electrode arrangement, where the counter electrode was a Pt mesh, the reference a Saturated Calomel Electrode (SCE = +0.244 V vs. NHE), and the tested specimen acted as the working electrode. The area of the working electrode exposed to the electrolyte solution was 15.9 cm^2 .

The potentiodynamic polarization curves were acquired by a Potentiostat/Galvanostat Solartron 1280 at a swept rate of 0.2 mV/s, over the range $\pm 0.250\text{ V}/(\text{SCE})$ from the corrosion potential (E_{corr}). The electrode potentials were stabilized for 10 min in the electrolyte solution before starting each test. The inhibitive efficiency ($E\%$) was calculated from the following equation [66]:

$$E\% = \left(j_{\text{corr}-0} - j_{\text{corr}-i} / j_{\text{corr}-0} \right) \times 100$$

where:

$j_{\text{corr}-0}$ is the corrosion current density of the bare galvanized steel sheet; and

$j_{\text{corr}-i}$ is the corrosion current density of the galvanized steel sheet protected by

the *i*-conversion coating.

The EIS tests were performed with a Solartron 1255 Frequency Response Analyser® (FRA) coupled to an Impedance Potentiostat-Galvanostat Omnimetra PG-19A®, and both controlled by the ZPlot®. The measurements were performed at the E_{corr} in the 10^5 to 10^{-1} Hz frequency range, as a function of the exposure time in the electrolyte solution. A sinusoidal signal with 8 mV of amplitude was applied, and the acquisition rate was 10 points/decade. The E_{corr} was recorded before and after the finishing point of each experiment to verify that the stationary requirement was obeyed.

The experimental spectra were fitted and interpreted on the basis of equivalent electrical circuits using the software developed by Boukamp [67]. All impedance measurements were carried out with the electrochemical cell inside a Faraday cage to reduce external interferences as much as possible.

Considering that the corrosion resistance of passivated materials depends on the production procedure, each test was performed on three replicates of each samples type, and the reported results in the following Tables and Figures are the average of them.

3. Results and Discussion

3.1. Chemical Physical Characteristics and Thickness Measurements

The identification symbol, description and thickness measurements of the investigated samples are summarized in **Table 1**. It can be observed that the samples present similar coating thickness. As it was not possible to obtain information about the passive layer thickness, the values shown in **Table 1** correspond to the total coating thickness (zinc + passive layer).

3.2. Polarization Curves

Potentiodynamic measurements were performed to study the corrosion behavior of electrogalvanised steel/conversion layer systems in comparison to the electrogalvanised steel sheets without treatment and in contact with aerated 0.05 mol/L NaCl or 0.1 mol/L Na_2SO_4 solution at $22^\circ\text{C} \pm 2^\circ\text{C}$. Four coating compositions were studied corresponding to the ZCe, ZCeD, ZCrZr and ZCr6 samples,

Table 1. Identification, description and coating thickness of the tested samples.

Identification	Description (zinc/conversion layer)	Average thickness of the Zn + conversion coating (μm)
Z	Zn without conversion treatment	9.47 ± 0.23
ZCe	Zn/Ce ³⁺	9.88 ± 0.39
ZCeD	Zn/Ce ³⁺ and Ce ⁴⁺	9.48 ± 0.75
ZCrZr	Zn/Cr ³⁺ + Zr complexes	10.82 ± 0.53
ZCr6	Zn/Cr ⁶⁺	11.12 ± 0.56

respectively. The potentiodynamic curves are shown in **Figure 1(a)** and **Figure 1(b)**, and both the corrosion potential (E_{corr}) and corrosion current density (j_{corr}) values obtained from the Tafel extrapolation method are collected in **Table 2**. It also presents the calculated polarization resistance (R_p) and protective efficiency percentage ($E\%$) values offered by each of the investigated samples.

Potentiodynamic curves obtained in aerated 0.05 mol/L NaCl solution for all the tested surface conditions are displayed in **Figure 1(a)**. The results show similar anodic and cathodic characteristics for the bare zinc coating (Z), or those covered ZCe or ZCeD conversion layers, with a slight polarization of the cathodic reactions and a strong dissolution tendency in the anodic ones. For these samples type, the main cathodic reaction (oxygen reduction) produces OH^- ions,

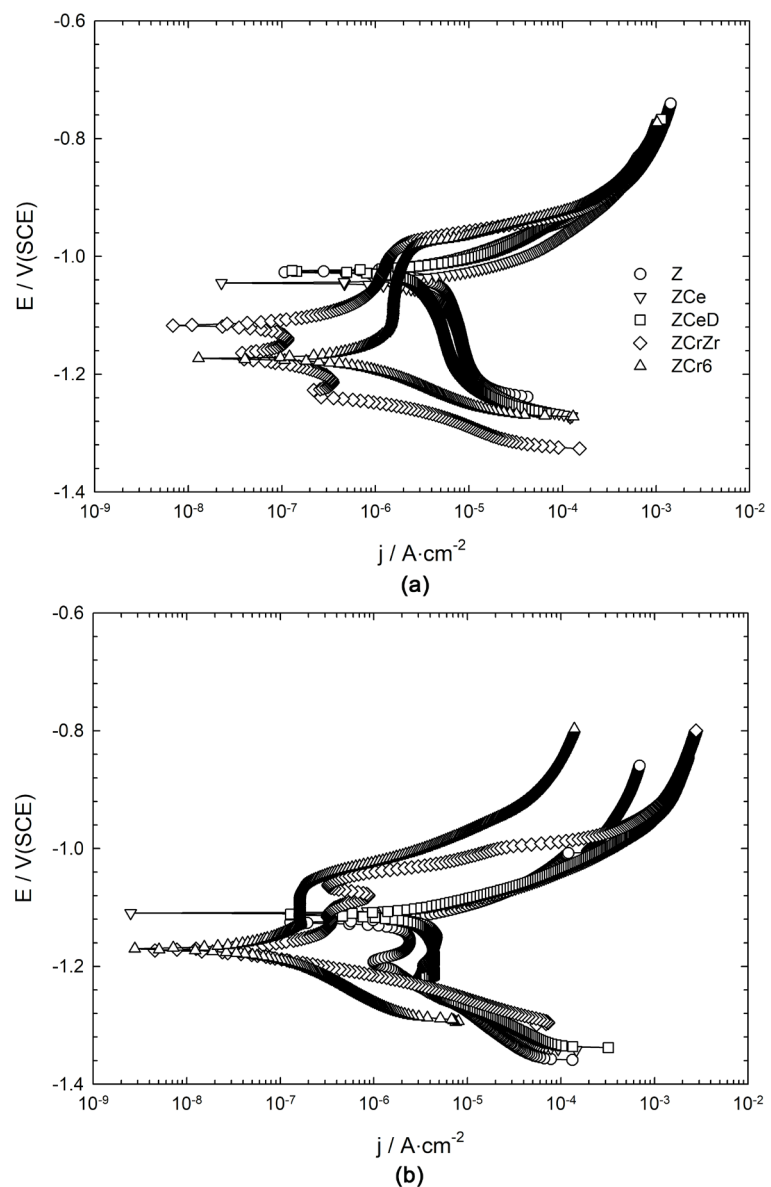


Figure 1. Polarization curves for the electrogalvanized samples without or with surface passivation treatments. Electrolyte: (a) 0.05 M NaCl solution; (b) 0.1 mol/L Na_2SO_4 .

which react with the Zn^{2+} coming from the anodic areas to form zinc corrosion products. These, combined with the Cl^- electrolyte ions, lead to the formation of Simonkolleite and/or other zinc-chloride charged ions [68] [69] and, as a consequence, to a certain diffusional controlled tendency, which indicates that in Cl^- medium these sample types are more inclined to inhibit the cathodic reaction due to the high water permeability and porous nature of the protective layers [70] [71] [72] [73]. Both the pure zinc coating and the conversion layers defects lead to anodic depolarization, whereas the conversion layer deposition on partial substrate areas would be the reason for the slight cathodic polarization reaction on the ZCe and ZCeD samples.

On the contrary, the anodic and cathodic branches of the ZCrZr and ZCr6 samples presented significant differences regarding the above tested samples. The E_{corr} value of the chromium treated samples was comparatively more negative than the measured in the other ones. Their potentiodynamic curves show that after an active dissolution the ZCrZr and ZCr6 samples revealed a passive behavior until approximately -0.96 V/SCE when the passive film formed on both sample surfaces was broken causing the restarting of the substrate active dissolution. As well, the cathodic polarization curves of the ZCr6 samples indicated an activation control, while the corresponding to the ZCrZr samples was very different.

The results also show that the reaction mainly depolarized by the chromate formed passivating film was the cathodic one. A comparison of the ZCrZr and ZCr6 treatments reveals that the first was related to much lower anodic or cathodic current densities and presented a corrosion potential whose current density ($<10^{-6}$ A·cm $^{-2}$, **Table 2**) is typical of passive materials. This indicates that

Table 2. Electrochemical parameters obtained from polarization curves.

Sample	E_{corr} (V/SCE)	j_{corr} (A/cm 2)	R_p (Ω /cm 2)	$E\%$
0.05 mol/L NaCl				
Z	-1.026	1.52×10^{-5}	232.43	-
ZCe	-1.046	1.73×10^{-5}	213.47	13.82
ZCeD	-1.025	1.28×10^{-5}	343.50	15.79
ZCrZr	-1.118	5.61×10^{-7}	6143.40	96.32
ZCr6	-1.172	2.06×10^{-6}	1405.70	86.45
0.1 mol/L Na $_2$ SO $_4$				
Z	-1.127	1.25×10^{-5}	272.52	-
ZCe	-1.111	1.19×10^{-5}	252.24	4.80
ZCeD	-1.113	1.44×10^{-5}	277.21	-15.2
ZCrZr	-1.173	4.71×10^{-7}	9407.20	96.24
ZCr6	-0.930	2.31×10^{-7}	13569.00	98.16

potential instabilities due to environmental changes in the potential range until passive film breakdown does not lead to highly corrosive and harmful conditions once the passive film stays on the surface, showing that it is a highly protective film. The lowest anodic and cathodic current densities associated to this type of sample show that the conversion layer polarizes the anodic and cathodic reactions, although its breakdown resistance was like the ZCr6 coating. The high corrosion protection that the ZCrZr film afforded to the substrate could be due to the Zr component, however, the Cr^{3+} component plays an important role contributing to the enhancement of the barrier properties.

Polarization curves obtained in aerated 0.1 mol/L Na_2SO_4 solution at ($22^\circ\text{C} \pm 2^\circ\text{C}$) for all the tested surface conditions are presented in **Figure 1(b)**. As seen in **Figure 1(a)**, de DC data obtained on zinc (Z) and coated samples (ZCe or ZCeD) confirm that these conversion layers do not significantly affect the electrochemical behavior of the electrogalvanised steel. Therefore, it is possible to assume that the Ce-based conversion layers produced in both cases cannot protect the electrogalvanised steel as a barrier. On the contrary, the ZCrZr and ZCr6 samples show a noticeable j_{corr} decrease, **Table 2**. In that sense, the anodic and cathodic characteristics of ZCrZr and ZCr6 samples presented large differences from the Z ones. As seen, reduction of the anodic slope and shifting of E_{corr} towards more cathodic domains occurs. The higher barrier properties provided by the ZCrZr coating can be ascribed to both the stability and presence of Cr_2O_3 and Zr complexes, respectively.

3.3. Impedance Measurements

Examples of the impedance spectra in Bode form obtained at different exposure times in aerated 0.05 mol/L NaCl or 0.1 mol/L Na_2SO_4 solution at ($22^\circ\text{C} \pm 2^\circ\text{C}$) are shown in **Figure 2** and **Figure 3**, respectively.

Figure 2 displays the impedance evolution of electrogalvanised steel samples, either without or with passivation treatments, after potential stabilization in aerated 0.05 mol/L NaCl solution. Two time constants were indicated in the impedance spectra of the untreated electrogalvanised sample, the one at the higher frequencies (HF) likely due to the presence of zinc corrosion products, and the one at the lower frequencies associated to charging of the electrochemical double layer in parallel with the charge transfer processes at the zinc/solution interface. The HF time constant dislocated into lower frequencies with the immersion time, due to the slowing down of the dissolution processes as result of the increasing zinc corrosion products formed on the electrogalvanised surface. Similar effects were obtained for ZCe or ZCeD samples, however, for these last samples types, the second time constant at lower frequencies are not well defined. Besides, the electrochemical response of a Ce conversion layer, usually seen at high frequencies was not identified on neither of the two types of the tested Ce surface coatings.

The impedance spectra for ZCrZr samples show higher impedance values

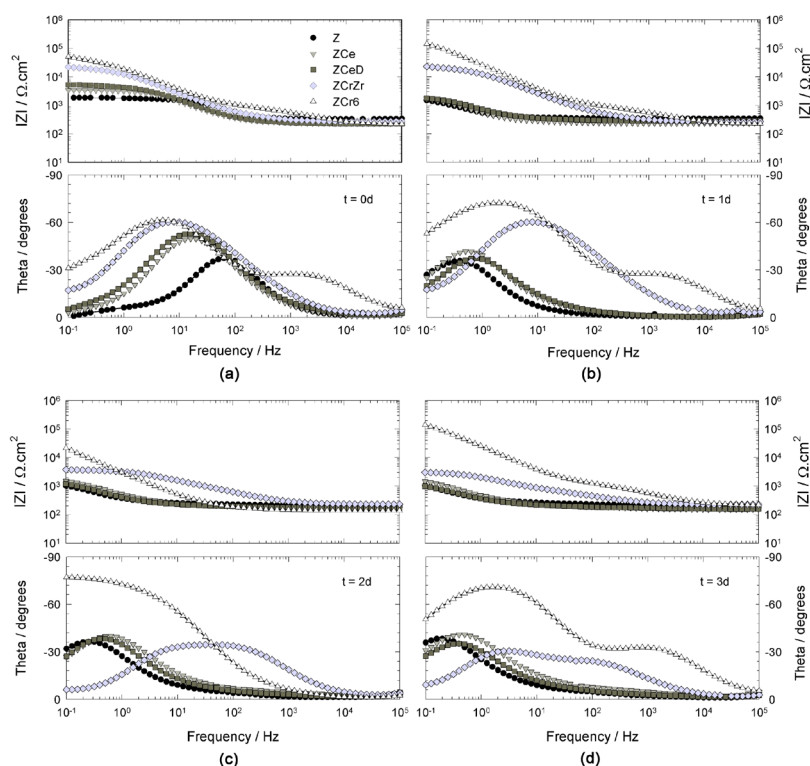


Figure 2. Effect of immersion time in naturally aerated 0.05 mol/L NaCl solution on the Bode plots of the tested samples at (a) 0 d; (b) 1 d; (c) 2 d; and (d) 3 d.

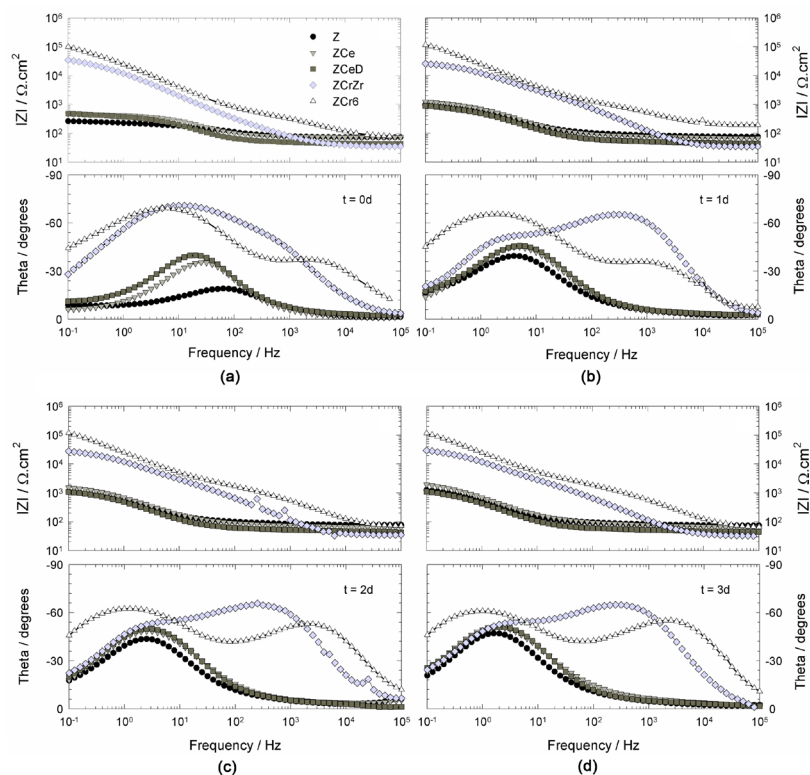


Figure 3. Effect of immersion time in naturally aerated 0.1 mol/L Na₂SO₄ solution on the Bode plots of the tested samples at (a) 0 d; (b) 1 d; (c) 2 d; and (d) 3 d.

associated to these samples compared to the other tested surface treatments, and the protection afforded lasted for longer periods than for the previous ones. The protection afforded lasted for at least 1 d and deteriorated between 1 and 2 d in the exposed ZCrZr samples, whereas for the ZCr6 samples the protection afforded increased with time until 1 d, likely due to precipitation of protective products on the surface, characteristic of this type of layer, being fairly stable until 3 d when the test was concluded. For these two treatments, two time constants were identified, being clearly separated for the ZCr6 samples. These results show that the protection afforded by the Cr(VI) conversion layer not only was greater than the provided by the ZCrZr layer containing trivalent chromium and fluorzirconium particles, but also offered longer duration.

Figure 3 exhibits the evolution of the electrogalvanised steel samples impedance spectra, either without or with passivation treatments, after potential stabilization in aerated 0.1 mol/L Na₂SO₄ solution. This Figure shows that the ZCrZr and ZCr6 samples provided the largest impedance (over almost the frequency range) while the Z, ZCe and ZCeD samples presented lower and very similar impedance values for the 3 days of immersion. Also, in this electrolytic medium the Bode diagrams show at least two well-defined time constants at the different immersion times tested. However, the deconvolution of these diagrams through the fitting program showed that, in some cases, there were overlapping time constants (not detectable by naked eye), which is why their number could be greater than 2. In accordance with the results obtained in the DC tests, the higher barrier properties provided by the ZCrZr coating can be ascribed to both the stability and presence of Cr₂O₃ and Zr complexes, while the corresponding to the ZCr6 samples to the effective passivating action offered by the Cr(VI)-based bath.

In this study, the impedance data of pure zinc coating, and the Cr(III) + Zr complex layer, Ce(III) layer, Ce(IV)/Ce(III) double layer or Cr(VI)-treated surfaces can be fitted by the complete or partial version of the equivalent circuit proposed in **Figure 4**. In this equivalent circuit, R_s represents the electrolyte resistance, R₁ the resistance to the ionic flux in the pore and C₁ the dielectric capacitance of the conversion layer. The R₂ and C₂ parameters account for the charge transfer resistance and the electrochemical double layer capacitance of the corrosion process, respectively [19] [74]. As immersion time and zinc dissolution increases, corrosion products could accumulate at the bottom or within the pores. In such circumstances, their contribution to the system impedance would be characterized by the R₃ and C₃ parameters [19] [74]-[80]. The diffusion component W obtained at certain exposure times was associated with an oxygen diffusion-controlled reaction usually found in zinc corrosion [81] [82].

The values of the R₁, C₁, R₂, C₂, R₃, and C₃ parameters estimated from the analysis of the impedance spectra fitting as a function of immersion time in 0.05 mol/L NaCl or 0.1 mol/L Na₂SO₄ are reported in **Figures 5(a)-(e)** and **Figures 6(a)-(g)**, respectively.

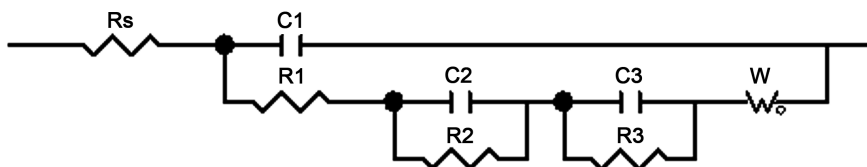


Figure 4. Equivalent circuits used to model the experimental impedance data of the tested samples as a function of the immersion time in naturally aerated 0.1 mol/L Na_2SO_4 or 0.05 mol/L NaCl solutions.

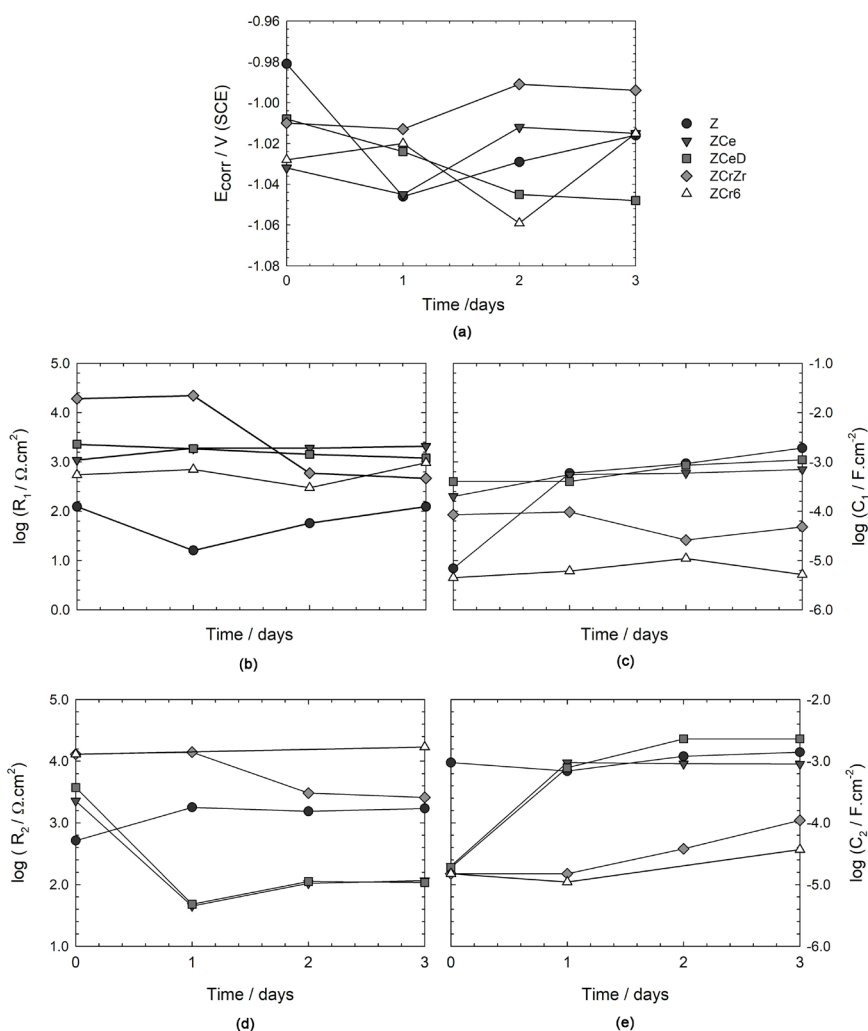


Figure 5. Time dependence of the resistive-capacitive components of the impedance corresponding to the tested samples immersed in naturally aerated 0.05 mol/L NaCl for 3 d.

3.4. Evolution of Samples, E_{corr} and Impedance Components with the Immersion Time

Figures 5(a)-(e) show the evolution of the E_{corr} and each component of the equivalent circuit as a function of immersion time of the bare or coated electro-galvanised steel sheets in contact with naturally aerated 0.05 mol/L NaCl solution.

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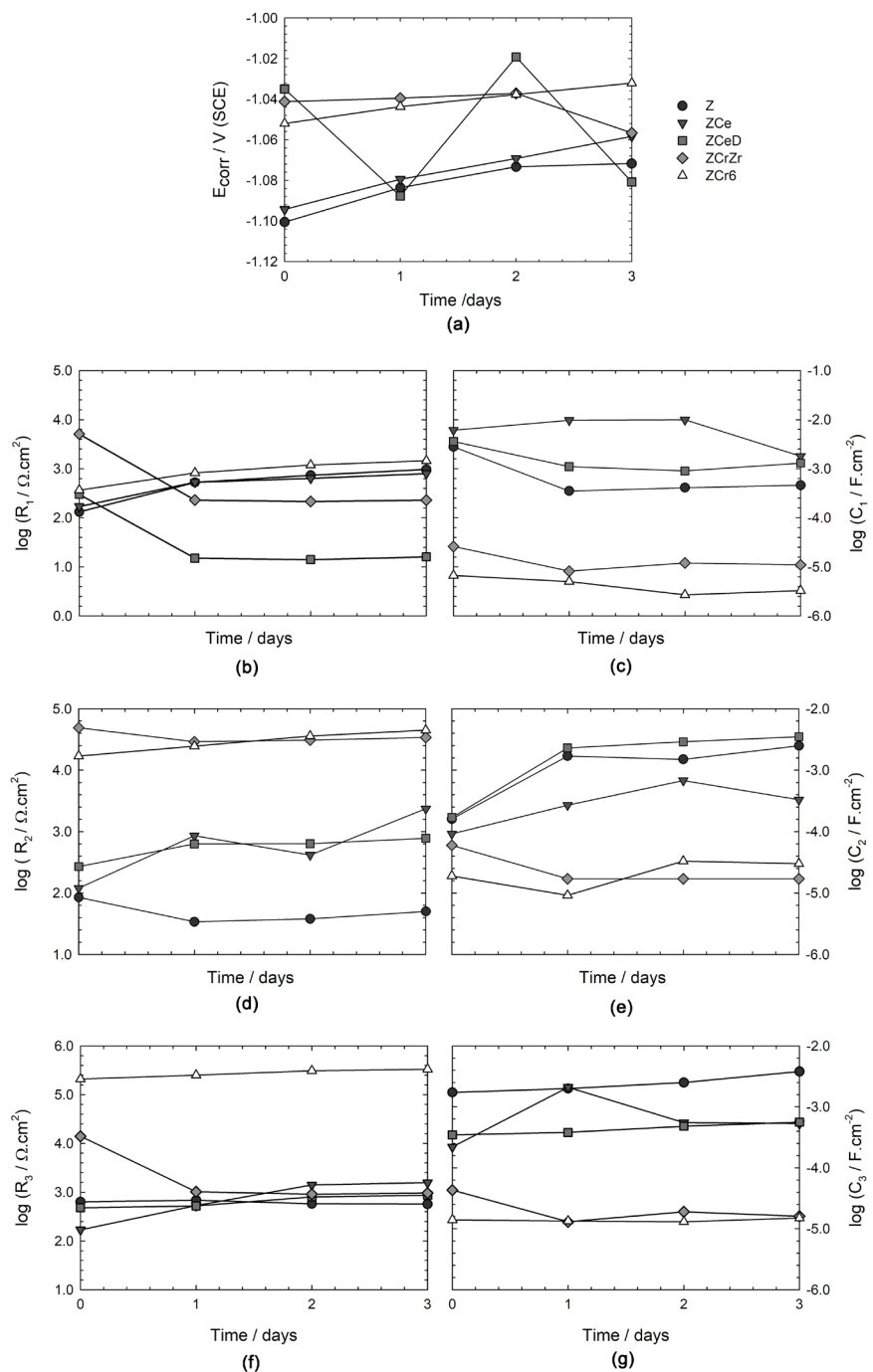


Figure 6. Time dependence of the resistive-capacitive components of the impedance corresponding to the tested samples immersed in naturally aerated 0.1 mol/L Na₂SO₄ solution for 3 d.

As previously mentioned, the poor barrier properties provided by the conversion layer made possible that the zinc corrosion reaction initiated just after immersion. In general terms, the displacements shown during the immersion test by the E_{corr} values corresponding to the different samples can be attributed to the

following effects: the decrease of such values were caused by the activation of the zinc areas at the bottom of the conversion layers defects (micropores, microcracks) due to their interaction with the Cl^- ions present in the electrolyte. The activation mechanism includes the replacement of the outer part of the zinc oxides by zinc corrosion products, which are less protective than the original oxides. This change enhances electrochemical reactions such as the zinc anodic dissolution. On the contrary, the displacement of the E_{corr} values towards nobler values observed for the different samples can be associated to the delay or polarization of the surface reactions between the electrochemically active areas of zinc and the electrolyte due to certain protective capacity developed by the corrosion products on the zinc surface and/or within and at the bottom of the conversion layers defects. This is to attenuate the zinc dissolution rate (anodic reaction) and/or the diffusion of oxygen to cathodic zones.

The results obtained from the fitting procedure described in the above paragraph are shown in **Figures 5(b)-(e)**. The chi squared (χ^2) value for the fitting was $\leq 5 \times 10^{-4}$ (the smaller this value is, the closer to fit to the experimental data).

Suzuki and Venkatesan [83] [84] studied the corrosion products of zinc in Cl^- media. According to these authors, zinc is always covered by a ZnO layer and, depending on the environment humidity, $\text{Zn}(\text{OH})_2$ may also be present, which act as a protective barrier preventing corrosion. During the exposure to the aerated 0.05 mol/L NaCl solution for 72 h one interesting observation was that the corrosion of the Z samples was reasonably localized, *i.e.* it started at small areas and then it changed from side to side along the surface. The corrosion process started with the attack of the zinc oxide/hydroxide barrier by the action of H_2O and Cl^- ions and zinc dissolution occurred not in uniform way, but in local areas.

The more interesting data to discuss are the resistance of the chemical conversion layer R_1 (giving information on the barrier properties of this layer) and the charge transfer resistance R_2 (giving information on the kinetic of the corrosive process). An example of evolution of the coating resistance (R_1) for the Z samples is in **Figure 5(b)**. The same Figure shows that the resistance provided by the ZCrZr and ZCr6 pretreatments offers a higher protection, in comparison with the ZCe and ZCeD pretreatments.

Particularly for the ZCr6 samples along throughout the test, and for the ZCrZr for the first day of immersion, this fact has a strong influence on the charge transfer resistance and therefore on the corrosion rate (**Figure 5(d)**). Generally, the decrease of R_1 (**Figure 5(b)**) and increase of C_1 (**Figure 5(c)**) indicates that the blocking performance of the conversion layer has been gradually disappearing [17] [85]. The decline of the anticorrosive performance is attributed to local microcracks formed on the conversion-coating layer. Comparing with the initial stage, the microcracks have propagated throughout the coating surface during the immersion. On the contrary, the trend of the resistance inside the defects (R_1) to show certain increase and/or of the coating capacitance (C_1) to decrease can be related to the formation and gathering of the zinc corrosion

products.

During the same testing time, the evolution of R_2 values (**Figure 5(d)**) reflect the variability of the active surface where corrosion occurs and, hence, the protection effectiveness. In that sense, it is remarkable that passivation-activation can occur simultaneously on the zinc surface with different extension. The higher protection efficiency for the 3 days of immersion was provided by the ZCr6 pretreatment due to the passivation action of the mobile Cr^{6+} ions available in the coating, followed by the ZCrZr whose protective action has been attributed to both the Zr and the Cr^{3+} components, as it was established when discussing the results with DC. On the other hand, the R_2 values in the ZCe and ZCeD samples dropped drastically during the first day of immersion but then remained almost constant until the end of the test. In all the cases, the presence of a plateau region during the test indicates that a dynamic equilibrium between the anodic and cathodic reactions is reached and suggest a lateral surface coverage of the conversion coating.

The increasing of R_2 means that the charge transfer resistance between the zinc and the solution becomes more difficult due to the passivation property afforded by the corresponding conversion coating layer during the immersion. The decreasing of R_2 indicates a progressive drop of the protection provided by the conversion layer. The C_2 values (**Figure 5(e)**) are proportional to the area involved in the electrochemical reactions, *i.e.*, the area of microcracks in contact with the solution. Therefore, an increasing indicates that the corrosion inside the microcracks becomes more severe and the microcracks area increases with the immersion time.

Figure 6 shows the evolution of the E_{corr} (a), and of each component obtained from the impedance data deconvolution (b-g) for pure or coated electrogalvanised steel sheets immersed for 3 days in naturally aerated 0.1 mol/L Na_2SO_4 solution. As seen in **Figure 6(a)**, in comparison with the changes in the E_{corr} values obtained for the samples tested in contact with NaCl, the measured for their replicates for the same testing time in Na_2SO_4 solution were much less important. In this case, the most significant displacement (± 0.060 V/SCE) occurred in the ZCeD sample, while in the rest, a shift mostly towards slightly more positive values took place. This shift is concern with a slow increase in the amount of corrosion products within the conversion layers defects, which act as a diffusion barrier to ions such as SO_4^{2-} through the conversion layer. However, with the increasing of the immersion time it can be expected that the corrosion inside the defects of the conversion layer become more severe and the cracks occurs, this was may be what happened with the ZCeD samples. Another possibility is that the corrosion products inside the defects loosened and diffuse towards the solution. In this case, the barrier effect is lost, and zinc dissolution is increased, generating new corrosion products and, therefore, a new barrier effect that reduces the electrochemically active areas making that the E_{corr} moves towards nobler values.

In **Figure 6(b)** it is possible to note an increase of the conversion layer resistance (R_1) values along the 72 h of immersion for the Z, ZCe and ZCr6 samples. On the contrary, those corresponding to the ZCeD and ZCrZr ones decreased within the first 24 h but then remained constant up to the end of the test. As seen, the R_1 values were mostly greater for the Z, ZCe and ZCr6 than those for the ZCeD and ZCrZr samples. Despite this, the charge transfer resistance (R_2) (**Figure 6(d)**) values not only for the ZCr6 but also for the ZCrZr samples were greater than those for the ZCe and ZceD samples, and all of them higher than for the Z ones. This means that to a greater or lesser extent all the conversion coatings were able to reduce the zinc corrosion rate throughout the test. It is assumed that the particularly anomalous behavior of the ZCrZr samples, this is low R_1 but high R_2 values, could be because the local microcracks formed on this conversion layer do not affect its very effective passivating effect.

The dielectric capacity (C_1) evolution for the pure zinc (Z) and the four conversion films tested is shown in **Figure 6(c)**. In this the C_1 value remained nearly constant for all the samples, but also that it was almost two orders of magnitude smaller for the better and more protected ZCr6 and ZCrZr samples. This consistency throughout the test was attributed to the fact that once the conversion layer microdefects were full of solution, both the microdefects number and size as well as the dielectric constant value of the electrolyte accumulated inside them remained unchanged.

The electrochemical double layer capacity (C_2) initially increased with the immersion time but then remained almost stable for the Z, ZCe, and ZCeD samples, **Figure 6(e)**. As occurred with the coating dielectric capacity (C_1), the C_2 value was less for the ZCr6 and ZCrZr than for Z, ZCe, and ZCeD samples. The C_2 value is proportional to the area involved in the electrochemical reactions, *i.e.* the area of microdefects in contact with the electrolyte. Therefore, changes in C_2 indicate that the corrosion inside of such microdefects become more severe if the electrochemically active areas increase, or else that these latter decrease due to the gathering of corrosion products within and/or the bottom of those microdefects. Finally, another possibility is that its value remains constant if the anodic areas/cathodic areas ratio does not change, as mostly occurred in the case of the ZCr6 and ZCrZr samples.

The time constant (R_3C_3) at the lowest frequency region corresponds to the corrosion products formed in the micropores or microcracks of the conversion layer. Its presence indicates that the conversion coating has been penetrated by the corrosive medium and corrosion reacts on the zinc coating. Again, the stability over the time as well as the higher R_3 and lower C_3 values (**Figure 6(f)** and **Figure 6(g)**) evidence that the conversion layer based on Cr(VI) provided the best protective behavior against the pure zinc corrosion in such an aggressive environment for this last metal as it is that containing SO_4^{2-} ions. **Figure 6(f)** also shows that except at the beginning of the test, after 24 h of immersion in 0.1 mol/L Na_2SO_4 solution, the resistive behavior of the corrosion products formed in the Z, ZCe, ZCeD, and ZCrZr samples was similar and constant. As it hap-

pened with the evolution of the parameters discussed in the previous paragraphs, the R_3 values stability is indicative that, for these exposure conditions, the corrosion process as well as the blocking action exerted by the corrosion products reached a steady state that lasted until the end of the test. The contribution of the corrosion products capacity (C_3) to the impedance of each tested sample is shown in **Figure 6(g)**. As seen, the C_3 values did not change significantly; this suggests that the surface area of the corrosion products in contact with the electrolyte neither did it throughout the 72 h of immersion. According to the results obtained with all the resistive and capacitive parameters contributing to the impedance measured for each sample as a function of the immersion time, after a short time of initiation the corrosion processes developed in each of them reached a relative and permanent steady state.

4. Conclusions

The potentiodynamic polarization and EIS techniques allowed the evaluation of the protective efficiency for the tested systems, which was different depending on the conversion layer formulation used to protect the electrogalvanised steel sheets.

The electrochemical behavior of the coated electrogalvanised steel sheets under immersion conditions could be modelled using a different number of time constants hierarchically distributed considering the presence of the conversion layer and both its microcracks and the corrosion products deposited in them. The high frequency time constant (R_1C_1), was related to the dielectric properties of the conversion layer; the second time constant (R_2C_2) refers to the zinc corrosion process, while the third one (R_3C_3) was associated to the presence and dielectric behavior of the zinc corrosion products. The evolution of these parameters pointed out that: 1) in contact with the 0.05 mol/L NaCl solution the higher protection efficiency was provided by the ZCrZr-based coating (96.32%) followed by the ZCr6-one (86.45%), while the less effective corresponded to the ZCe and ZCeD-based coatings, 13.82% and 15.79%, respectively; and 2) in the 0.1 mol/L Na_2SO_4 solution, the afforded protection degree by the ZCrZr and ZCr6 coatings was again very significant, 96.24% and 98.16%, respectively, but almost negligible (4.80%) by the ZCe-one. An opposite effect to the expected one presented the ZCeD coating since its presence accelerated the corrosion rate of the base substrate by an estimated value of 15.2%.

Although the presence of chromates, particularly those based on hexavalent chromium Cr(VI), remains at the forefront as a corrosion inhibitor of the steel family, the intense research carried out in different laboratories around the world to replace them with other types of coatings being more friendly to the human health and the environment is providing more and more encouraging knowledge. As examples of this, results produced by studies like the one here presented show that new and complex formulations based on a range of rare-earth metal (La, Y, Nd, Gd) salts were shown to be good corrosion inhibitors, acting by reducing the cathodic oxygen reduction reaction. In the same

way, organic carboxylate compounds (such as salicylate and cinnamate) at relatively high concentrations, were found to be efficient anodic inhibitors by forming a protective layer, mainly at the anodic sites.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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