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Experimental design for improvement of electrodeposited silane/zinc coating

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Abstract

This work presents a central composite design as a statistical tool to provide knowledge regarding the effect of variables that influence the electrodeposition of sol-gel zinc/silane hybrid coatings. Such coatings were deposited on carbon steel samples by a combination of tetraethoxysilane (TEOS) and Zn^{2+}, functionalizing the film with cathodic protection, beyond its barrier protection. The influence of the amount of TEOS, concentration of zinc ions and electrodeposition potentials were evaluated. Polarization curves were made aiming at measuring corrosion currents using Tafel extrapolation plots. Surface and coating characterization were determined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Coating degradation was analyzed by visual observation of corrosion products after immersion. Results revealed that corrosion rate results led to saddle shaped response curves, highlighting the importance of variables combined effects to improve steel protection. Moreover, visual inspection of immersed specimens showed lower corrosion degree for combined film deposition when compared to samples deposited solely with zinc or silane precursor.

Keywords: Carbon steel, Hybrid coatings, Electrodeposited films, Zinc, Silane coating

1. Introduction

In recent years, research has focused on the production of silicon-based coatings using the sol-gel methodology in order to hinder corrosion on metallic surfaces. This effort aims to produce coatings that are more efficient, and that cause less impact on the environment. Despite that, silica-based sol-gel coatings can be quite porous, when compared to conventional painting systems, exposing the metallic material to the corrosive medium. Thus, the manufacture of hybrid coatings has been sought with the purpose of improving its anti-corrosion capacity, besides inserting an active protection.

Among the hybrid coatings produced in the literature, it is possible to highlight the ones combining silica and less noble metals, such as zinc, which perform the functions of barrier and cathodic protection, respectively. Wu, et al. (1) used films composed of organosilanes and zinc as a protective coating against corrosion on steel. In order to add the cathodic protection of zinc with the silane barrier effect and demonstrate that the film can be deposited by a simple method of electrodeposition, bisane-1,2-triethoxyethylethylene (BTSE) was used in the work.

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Following the same perspective, S. Alinejad (2) used ZnCl2 as a source of zinc as an additive for a film composed of tetramethoxysilane (TMOS) and 3-glycidoxypropyltrimethoxysilane (GPTMS). The focus of the study was a univariate analysis of the concentration of zinc ions, comparing electrochemical impedance spectroscopies to determine what has the best protection against corrosion.

Also, Nikpour, et al. (3) conducted a study proving that the addition of zinc cations and *Mentha longifolia* to a primer composed of tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and γ-glycidoxypropyltrimethoxysilane (γ-GPS), improving its resistance to corrosion. Both additives were used as corrosion inhibitors.

Although it has already been reported in literature, such hybrid coatings present only univariate analyzes of the potential for electrodeposition and zinc concentration. Thus, the present work aims to explain the combined effect of the main variables associated with the electrodeposition process of hybrid coating based on silica and zinc in the control of carbon steel corrosion, in addition to determining its improved conditions.

2. Methodology

• Central Composite Design

The variables deemed as highly capable of influencing film deposition and its protection in NaCl 3.5% wt. was the electrodeposition potential, concentration of Zn^{2+} and the amount of silane precursor in the deposition solution. Since zinc ions were obtained by the dissolution of $Zn(NO3)_2$, the evaluated variable was its concentration. Similarly, the silane precursor was Tetraethoxysilane 97% (Sigma-Aldrich) and the evaluated variable was the volume added to the deposition solution.

A central composite design (CCD) was carried out using the software Design Expert and considering the corrosion current as response variable. Its value was further minimized to obtain the conditions where barrier effects were more relevant.

Table 1 shows the axial levels (α), the central levels (C) and the factorial levels (f) used in the experiment. The maximum and minimum conditions were assigned from preliminary tests, and from them the central levels were calculated, while the axial levels were selected by the Design Expert software, based on the values of the factorial levels.

Table 1 - Experiments of CCD (axial levels – α, central levels – C, factorial levels – f)

EXP	Potencial (V)	$[Zn(NO_3)_2]$ (mol/L)	TEOS (mL)
1 (f)	-1.3000	0.1000	2.0000
2 (f)	-1.3000	0.1000	5.0000
3 (f)	-1.3000	0.3000	2.0000
4 (f)	-1.3000	0.3000	5.0000
5 (f)	-1.7000	0.1000	2.0000
6 (f)	-1.7000	0.1000	5.0000
7 (f)	-1.7000	0.3000	2.0000
8 (f)	-1.7000	0.3000	5.0000

9 (α)	-1.2294	0.2000	3.5000
10 (α)	-1.7706	0.2000	3.5000
11 (α)	-1.5000	0.0647	3.5000
12 (α)	-1.5000	0.3353	3.5000
13 (α)	-1.5000	0.0000	1.4703
14 (α)	-1.5000	0.2000	5.5297
15 (C)	-1.5000	0.2000	3.5000
16 (C)	-1.5000	0.2000	3.5000
17 (C)	-1.5000	0.2000	3.5000

Blank samples are based on the parameters improved for minimum corrosion rate. Thus, they comprised coatings deposited only with TEOS, only with zinc and also the bare steel. It is important to mention that $NaNO_3$ was added in deposition solutions that did not contain zinc ions, compensating for the lack of zinc salt.

- **Solution and Sample Preparation**

The electrodeposition solution consisted of a mixture of 70.0 mL of ethanol 95%, 30 mL of $Zn(NO3)_2.6H_2O$ solution, and a volume of TEOS, whose concentration and volume varied according to the CCD experimental design shown in Table 1. The medium was then acidified with 1.0 mol/L HNO_3 to pH 3. The solution remained under stirring for 2 hours at approximately 300 rpm, to promote the colloid formation.

The metallic coupons where coatings were deposited were carbon steel SAE 1020 (C 0.19%; Mn 0.5%; Si 0.15%; P 0.023%; S 0.014%) with dimensions 2.0 cm x 1.5 cm x 0.6 cm. The sample were prepared with emery paper of 400, 600 and 1200, consecutively. The surfaces of the specimen were covered with tape, leaving only one face exposed (2.0 x 1.5 cm) where the hybrid films were deposited. After the surface preparation, the material was rinsed with ethanol, in order to avoid flash rust, and immersed in an ultrasonic bath of ethanol 95% for 5 min, in order to degrease the surface, being finally dried with of hot air.

- **Electrodeposition**

Electrodeposition was controlled by Metrohm's potentiostat PSGTAT302N, using an electrochemical cell composed of three electrodes: $Ag/AgCl_{sat}$ as reference, titanium sheet as counter electrode (11.32cm2) and the carbon steel alloy as a working electrode. The electrodes were immersed in the previously hydrolyzed solution and the electrodeposition was performed during 10 minutes, inside a Faraday cage, applying the specific potentials for each experiment according to Table 1. After electrodeposition, samples were immersed in distilled water and ethanol in order to remove poorly adsorbed sol particles and reduce tensions within the coating upon drying.

- **Immersion Test**

The coated specimens were immersed in NaCl 3.5% wt. in order to analyze and compare the formation of corrosion products on their surfaces within 20 hours, as well as a manner to establish the anticorrosive capacity of the coatings.

- **Potentiodynamic polarization**

Potentiodynamic polarization tests were performed in electrochemical cells with three electrodes similar to the ones described in the previous section, except the solution (NaCl 3.5%$_{wt}$). The measurements were performed by Metrohm's potentiostat PSGTAT302N inside a Faraday cage. The initial and final scanning potential values were -0.9 V and -0.2 V respectively, with a scan rate of 10^{-3} V/s and step of $5x10^{-4}$ V. The test began when open circuit potentials reached -0.7 V so all samples could be analyzed under the same potential. Furthermore, if polarization curves were taken immediately after immersion, all corrosion current results would indicate the zinc corrosion rate due to the high amount of zinc, and, therefore, samples would not be properly distinguished for the experimental design.

In this study, polarization curves were obtained in order to determine the corrosion current and to compare the barrier effect provided by the coating. Tafel extrapolation method was performed on the voltammetry curves, and the obtained corrosion rates were used as output parameter for the CDD experimental design.

- **Electrochemical impedance spectroscopy (EIS)**

Electrochemical impedance spectroscopy (EIS) measurements were performed in electrochemical cell similar to the ones described previously, with frequencies ranging from 10^5 Hz to 10^{-1} Hz and amplitude was set to 5.0 mV. The measurements were performed by Metrohm's potentiostat PSGTAT302N inside a Faraday cage and beginning after 20 minutes of potential stabilization.

3. Results and Discussion

- **Corrosion Rate**

Table 2 presents the results of each experiment of CCD and Table 3 presents the effects on the corrosion rate of main and quadratic variables, as well as their interactions, along with their respective p-values. Quadratic terms were the most significant factors (p-value ≤ 0.05) and presented the greatest statistical significance for the corrosion rate mathematical model. Such characteristic resulted in saddle shaped response surfaces, as shown in Figure 1.

The increase of independent variables exhibiting positive effects are expected to cause an increase on the response variable as well, while negative effects cause a decrease. P-values, on the other hand, are associated with the statistical significance of a factor. Since the significance level for this work was stablished as 0.95, factors with p-values greater than 0.05 are considered statistically not significant for a mathematical model capable of describing the system.

Equation 1 displays the mathematical model that expresses the expected corrosion rate according to the independent variables levels, with coefficient of determination (R^2) equal to 0.9511 and standard deviation of 0.0052 mm/year. This equation includes some statistically not significant factors, as it was presented in Table 3. Nevertheless, some of those factors were kept since its removal led to a decrease in the value of R^2 and R^2 adjusted, consequently impairing the model adjustment. The formulation of mathematical models allowed the identification of the experimental conditions that led to minimum corrosion rate within the studied ranges.

$$CR = -0.415187 + 0.0433569A - 0.906728B - 0.608719C + 0.002516\,AC - 0.005388A^2 + 2.19462\,B^2 - 0.202020C^2 \quad \text{(Equation 1)}$$

Where:

CR = Corrosion Rate;
A = Volume of TEOS (mL);
B = Concentration of $Zn(NO_3)_2$ (mol/L);
C = Electrodeposition Potential (V).

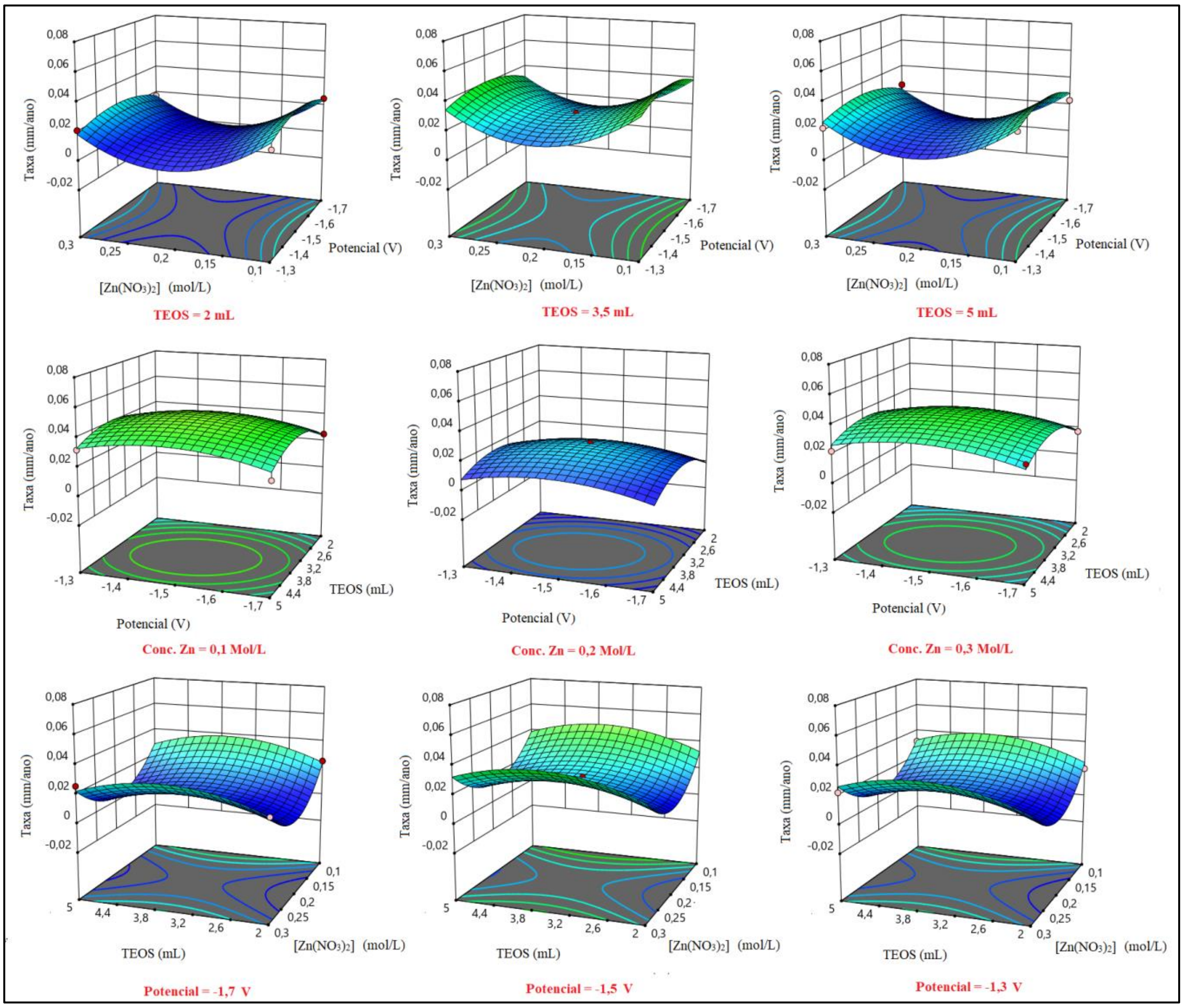
Table 2 - Results of CCD experiments

EXP	Corrosion Rate (mm/year)
1 (f)	0.0204
2 (f)	0.0317
3 (f)	0.0209
4 (f)	0.0220
5 (f)	0.0251
6 (f)	0.0233
7 (f)	0.0173
8 (f)	0.0255
9 (α)	0.0139
10 (α)	0.0334
11 (α)	0.0736
12 (α)	0.0562
13 (α)	0.0139
14 (α)	0.0091
15 (C)	0.0211
16 (C)	0.0187
17 (C)	0.0231

Table 3 – P-value and Effects of each Parameter and Combination

Factor	Effects	P-value
Intercept	0,0227	0,0850
A (TEOS volume)	0,0031	0,1983
B ([Zn $(NO_3)_2$])	-0,0033	0,1263
C (Potential)	0,0012	0,5838
AB	-0,0000	0,9926
AC	0,0008	0,7417
BC	-0,0004	0,8492
A^2	-0,0121	0,0118
B^2	0,0218	0,0004
C^2	-0,0081	0,0496

Regarding the concentration of zinc nitrate, it could be expected that its lower level would lead to higher deposition of silica, higher barrier effect and, consequently, lower corrosion rate. However, Figure 1 points out that corrosion rate can be greatly reduced when the concentration of zinc nitrate is set to 0.2 mol/L (intermediate level). The control of TEOS volume provides even further reduction when it is set to the lower (2.0 mL) or higher (5.0 mL) levels. Also, lower cathodic deposition potentials produced coatings more capable of protecting the samples from corrosion.



TEOS = 2 mL

TEOS = 3,5 mL

TEOS = 5 mL

Conc. Zn = 0,1 Mol/L

Conc. Zn = 0,2 Mol/L

Conc. Zn = 0,3 Mol/L

Potencial = -1,7 V

Potencial = -1,5 V

Potencial = -1,3 V

Figure 1 - Response Surface Charts for Corrosion Rate

It should be noted that the result that indicates the lowest rate is the most favorable for the desired protection against electrolyte permeation. The best values indicated by the equation corresponds to 4.90 mL of TEOS, 0.20 mol/L of $Zn(NO_3)_2$ and -1..30 V of electrodeposition potential, showing that the volume of TEOS is close to the maximum value. The result can be explained by the amount of silane in solution being a decisive factor in increasing the barrier protection. That said, previous analysis shows that there is a possibility of a low corrosion rate with lower volumes of TEOS. This can be explained due to a relation between the concentration of silane and the potential for electrodeposition.

In a previous issued work, it was done an analysis of the cathodic potential effectiveness time provided by the presence of zinc on the hybrid coating deposited on the carbon steel (4). It can be pointed out the reduction of cathodic protection time when only zinc is deposited under the same conditions of the best value founded, indicating that the deposition of silane is also important to maintain the cathodic protection time provided by zinc. Besides that, it is possible to compare that higher electrodeposition potentials lead to more uneven coatings, but it also provides a higher cathodic protection and, consequently, greater corrosion protection.

- **Immersion Test**

Immersion tests were carried out for 20 hours for specimens with coatings deposited under the conditions which led to the lowest corrosion current and blank samples associated to such condition. Figure 2 presents the specimens before immersion in NaCl 3.5% wt., showing a clear difference between the formed coatings. The presence of zinc in the coating increases the light reflection intensity of the coating, since in Figure 2(2) the coating is opaque in relation to the others.

After 20 hours of immersion, the specimens presented the aspects highlighted by Figure 3. The numbers in each image represent the same specimens as in Figure 2. It is also possible to observe that the carbon steel samples without coating and only with a zinc deposit showed uniform corrosion over the entire metal, demonstrating that the zinc layer could not protect the iron in the steel through the entire 20 hours of immersion. It is worth noting that the TEOS coating Figure 3(2) showed less corrosion product compared to the coating with TEOS and zinc Figure 3(4).

It can be also observed that, despite the coating of the specimen coated with TEOS and zinc appears to be with a higher degree of corrosion, a layer that keeps the corrosion product contained was formed, protecting the metal. This explains the low corrosion rate in this case, obtained through the mathematical model previously established (0.0086 mm / year).

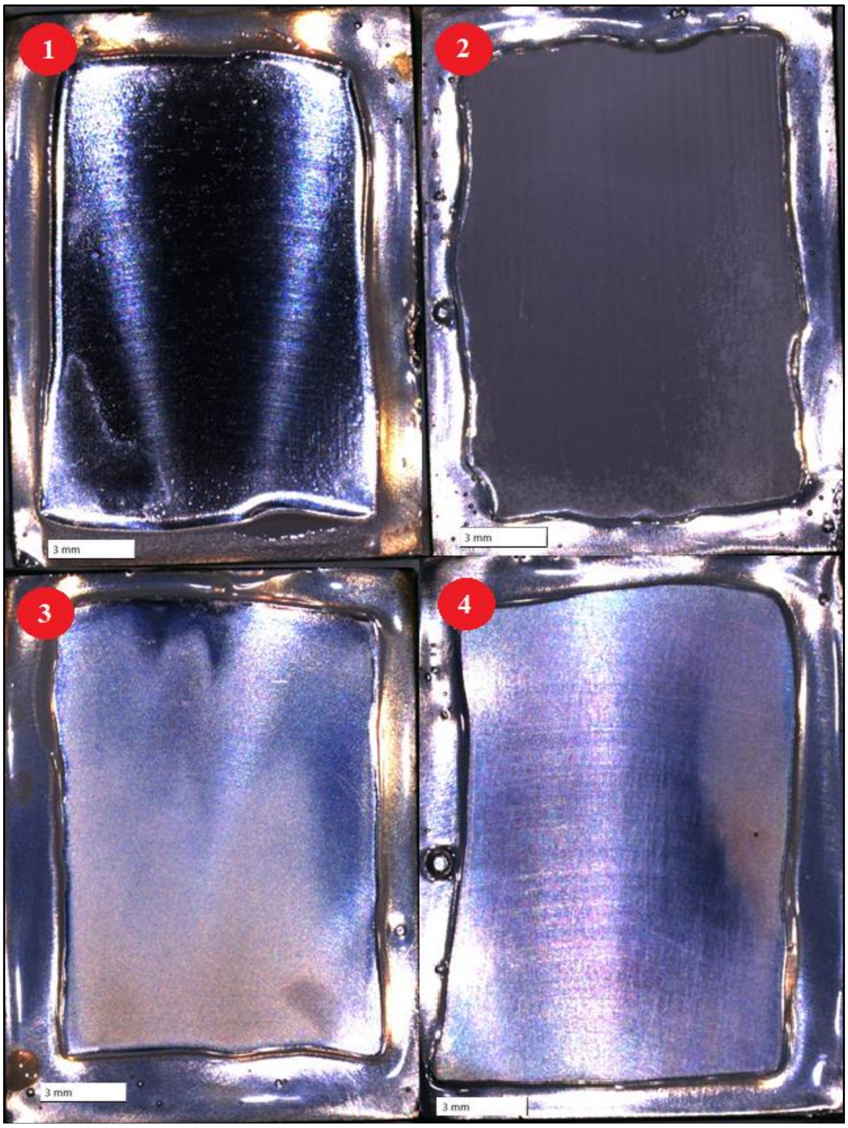


Figure 2 - Lower rate specimens before immersion (1 - bare steel; 2 - Coating only with TEOS; 3 - Coating only with Zinc; 4 - Coating with TEOS and Zinc)

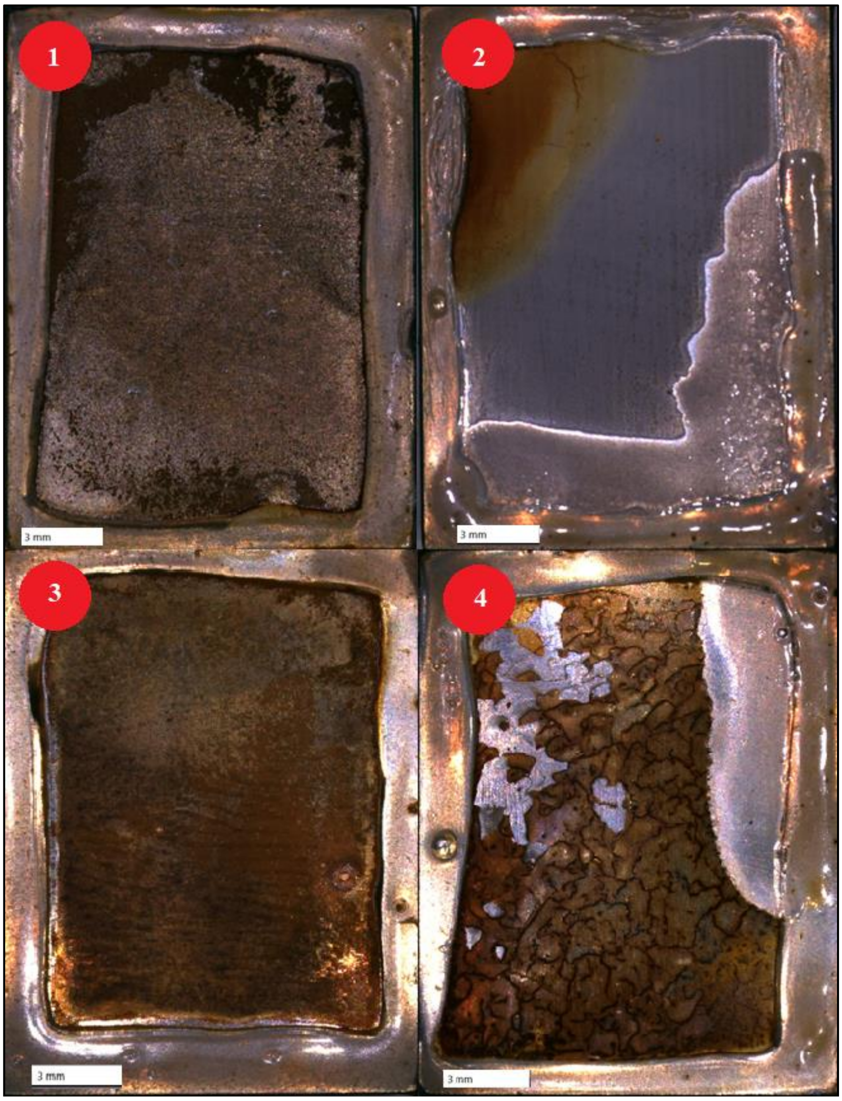


Figure 3 - Comparison between blank and lower rate coating (2 - Coating with TEOS only; 4 - Coating with TEOS and Zinc)

- **SEM/EDX**

Figure 4 presents the results of SEM and EDX of the coating deposited under the condition of minimized corrosion rate prior to the immersion in NaCl solution. It is possible to notice the film coverage and uniformity, despite the presence of some cracks even before the corrosive process. Such cracks are a result of internal tensions during coating drying. It can be also pointed out by Figure 4, the homogenous distribution of zinc, oxygen, carbon and silicon, provided by the mixture of TEOS and zinc as coating. Furthermore, the technique also detected iron due to the penetration of X-ray through the low film thickness.

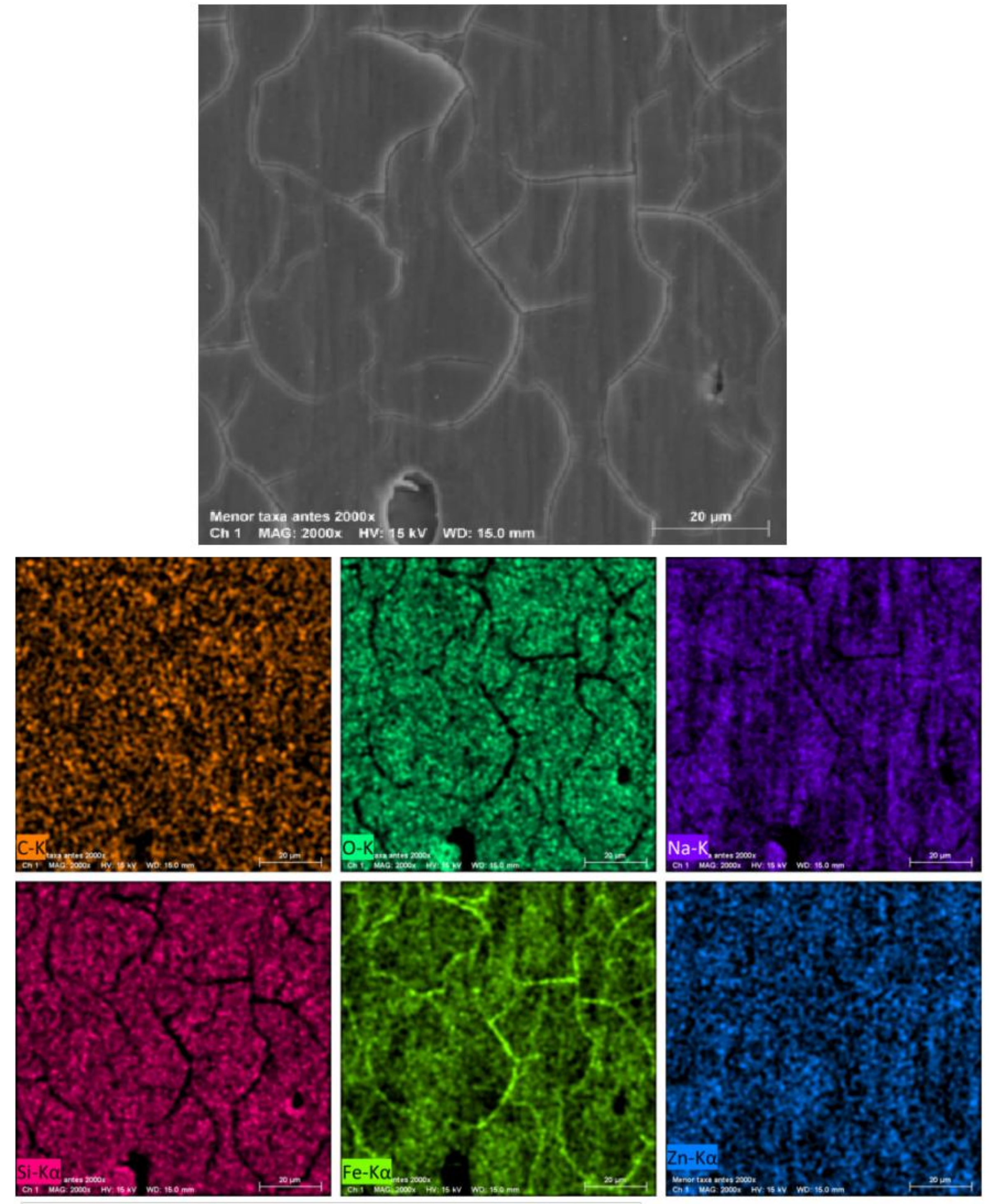


Figure 4 - SEM images and EDX elemental mapping of TEOS+Zn coating.

- **Electrochemical impedance spectroscopy (EIS)**

Figure 5 shows the evolution of impedance modulus (|Z|) over immersion time for the coated sample deposited under the conditions for minimized corrosion rate. It can be highlighted that during the earliest periods of immersion lower impedance modulus were detected due to the presence of zinc, which has a high tendency to oxidize. After zinc is mostly oxidized, barrier effects become predominant, increasing $|Z|_{0.1Hz}$ value, which can be detected after 60 minutes of immersion. It can also be pointed out that the $|Z|_{0.1Hz}$ decreased after 90 minutes.

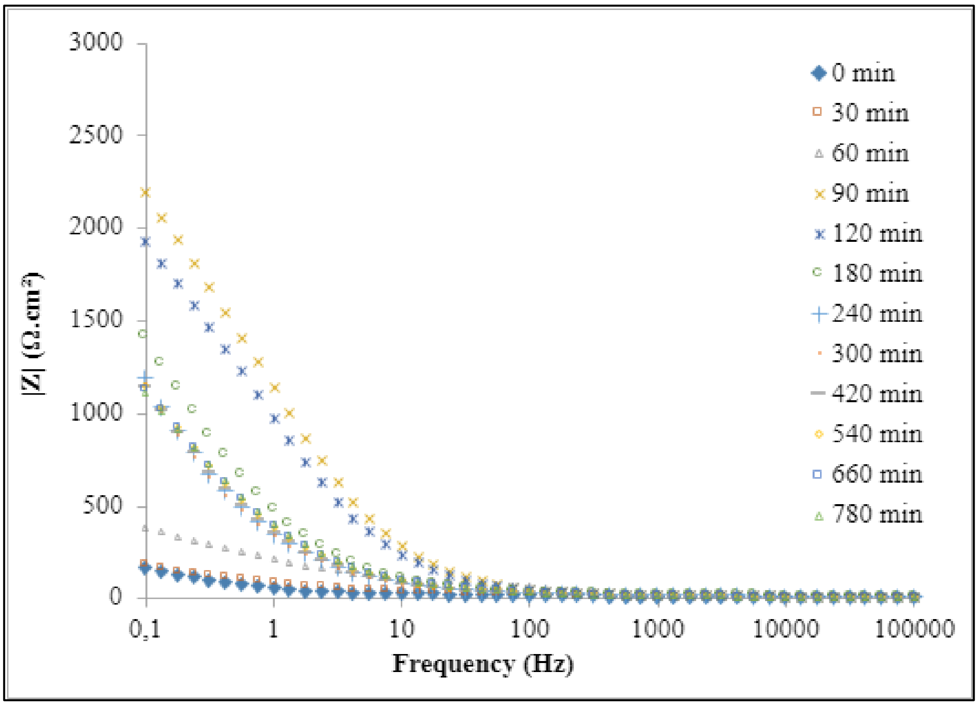


Figure 5 - Bode Plots for Coated Sample in NaCl 3,5% wt.

Figure 6 presents the phase angle plots for the coated sample. Results have demonstrated a fast zinc removal by oxidation and, as consequence, high frequency phase angles steeply increased in 90 minutes, indicating also an increase on the capacitive behavior of impedance, caused by the absence of zinc and presence of silica film. After 90 minutes of immersion, the high frequency phase angle profile presented continuously increasing values, which can be explained by the formation of steel corrosion products trapped on the porosity of the silica film, increasing its barrier effect. Such effect is exemplified by Figure 3(3) and 3(4), where rusty can be identified in areas where the silica coating did not delaminate.

Peaks presented in intermediate frequencies usually are caused by electrolyte diffusion through the coating, possibly due to the presence of irregularities (5)(6). So, the variation of phase angle after 120 min should be explained by the decrease of diffusion caused by the presence of corrosion products trapped in the coating porous.

Peaks in low frequency could be seen at the beginning of the experiment, due to the charge transfer of zinc and iron oxidation, probably due to the electrolyte’s diffusion (5)(7). After this, we could see a decrease of the phase angle explained by the absorption of the corrosion products in the film, improving the coating barrier effect

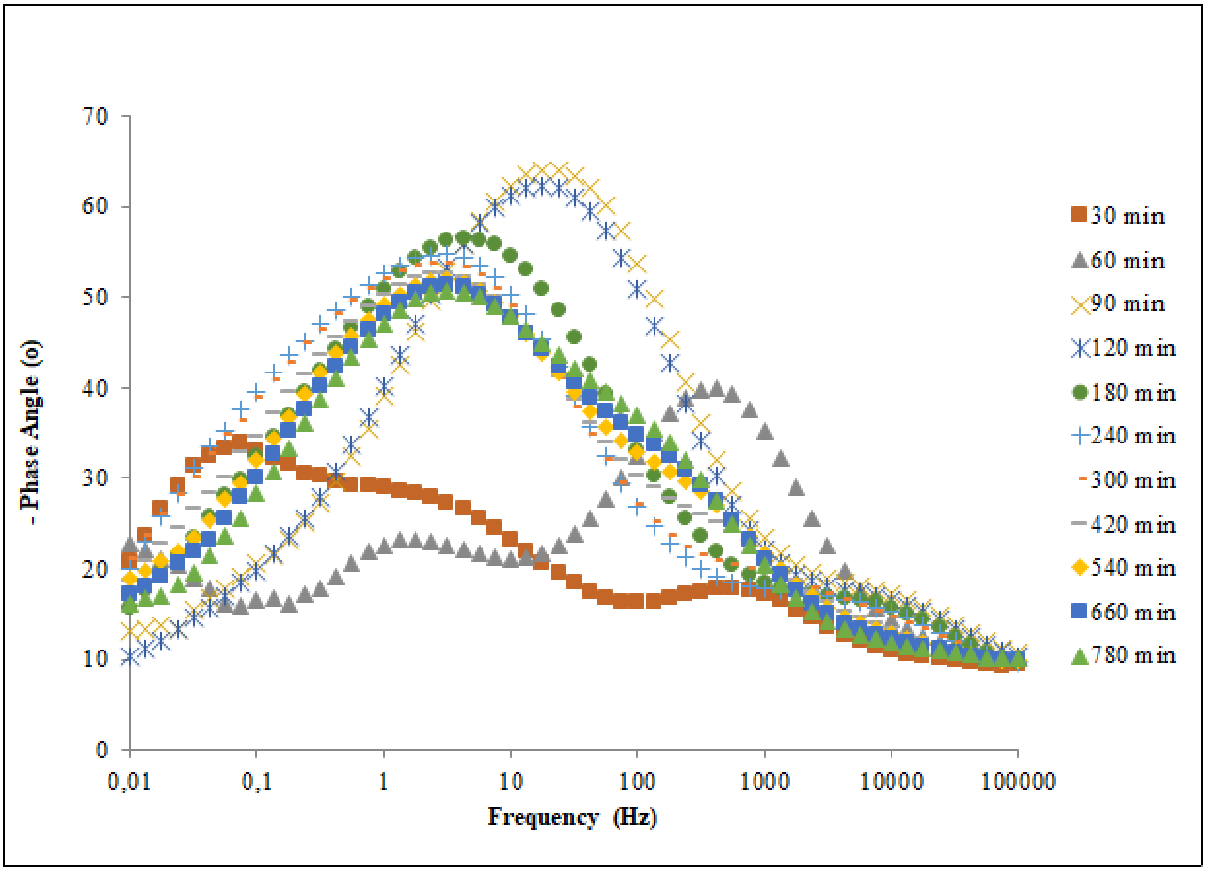


Figure 6 - Phase Angle Plots for Coated Sample in NaCl 3,5% wt.

4. Conclusion

The present work used an experimental design to determine the combined effect of the electrodeposition potential, $Zn(NO_3)_2$ concentration and TEOS volume in the corrosion rate. The design allowed the minimization of the corrosion current, caused by the combination of -1.30 V of deposition potential, 0.20 mol/L of $Zn(NO_3)_2$ and 4.90 mL of TEOS. Finally, analyzes were carried out comparing the best result with its respective blank samples, indicating that the coating composed by the silane and zinc mixture has better uniformity and protection against corrosion, contrasting with the films composed only by silane or zinc. From the results, it was possible to understand that the functionalization of silane coatings with zinc increases the efficiency of protection against corrosion of carbon steel SAE1020.

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5. Bibliographical References

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