

## Design with Anodic Dissolution Current as the Dependent Variable

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### Abstract

Galvanic corrosion between carbon steel and the shape-memory alloy CuAlBe was investigated. A fractional factorial design of  $2^{6-2}$  including 6 central points was used with the following variables:  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{HCO}_3^-$ , ratio of anodic to cathodic area (1:1, 1:0.5, 1:0.25) and temperature (25, 35 and 45 °C). The experimental design was used to investigate the main factors influencing the anodic dissolution current (dependent variable) as calculated from the galvanic current density. The dependent variable was directly proportional to the cathodic area, even in complex electrolyte solutions such as the water produced in mature oil wells. The experimental design provided information that could be used to minimize the dissolution of carbon steel. An analysis of the response surfaces showed that the area,  $[\text{SO}_4^{2-}]$  and  $[\text{HCO}_3^-]$ , and the  $\text{SO}_4^{2-} - \text{HCO}_3^-$  interaction significantly ( $p < 0.1$ ) influenced the anodic dissolution

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current. The relationship between the cathodic and anodic areas had the largest influence on the anodic dissolution current.

**Keywords:** galvanic corrosion, anodic dissolution, carbon steel, CuAlBe

## 1. Introduction

The petroleum industry faces a wide variety of conditions in its activities, which range from exploration to refining. Corrosion is one condition that often occurs in this industry, it is possible to state that it is also included among those conditions and this requires in-depth analysis. The electrolyte in corrosion in the petroleum industry is complex and highly saline. It contains CO<sub>2</sub> and H<sub>2</sub>S and is an aggressive corroding medium. The interaction between dissolved salts, corrosive gases and suspended solids, together with hydrocarbons and water in petroleum fields, results in a synergistic phenomenon of degradation of metallic materials that is still not fully understood [1,2].

Carbon steel is commonly used in engineering, and because it is relatively inexpensive, it is widely applied in oil production and refining (3, 4). In the petroleum industry, materials such as zinc (5), austenitic stainless steel (6), aluminum (7) are also commonly used in combination with carbon steel. Galvanic corrosion can occur where there is contact between carbon steel and other metallic materials.

Shape-memory alloys are metallic materials that demonstrate the capacity to return to a previously defined shape or size when subjected to an appropriate thermal cycle. Generally, these materials can be plastically molded at a relatively low temperature and, when exposed to a higher temperature, return to the form they had before molding (original form) [8]. One possible application of shape-memory alloys is in connection of steel pipes without the use of welding.

Because of the use of shape-memory alloys in the petroleum industry, galvanic corrosion between these alloys and carbon steel should be studied. Conventional isolation of each of them factors arduous and potentially inconclusive, as synergistic effects can occur that either retard or accelerate corrosion. Experimental design offers a practical way to study the factors that contribute to the corrosiveness of the aggressive medium encountered in the petroleum industry. It can be used to determine the main variables that significantly influence the corrosion process. Because of the number variables involved in this process, a fractional factorial design ( $l^{k-p}$ , where  $l$ =number of levels,  $k$ =number of factors, and  $p$ =size of the fraction of full factorial) can be used. A fractional factorial design can be used to assess the effects of the main variables with the same accuracy as a full factorial design [9].

The objective of this study was to develop an experimental design to study the main variables affecting galvanic corrosion between carbon steel and the shape-memory alloy CuAlBe in a complex fluid similar to that found in the oil and gas industry. In the present study, a two-level fractional factorial design of  $2^{6-2} + 6$  (central points) was selected for studying galvanic corrosion between carbon steel and the CuAlBe alloy in just 22 assays. This included 16 assays of a  $2^4$  design with six repetitions of the central point. By comparison, the corresponding full factorial design ( $2^6$ ) would require 64 assays. Because central point repetitions are essentially the same experiment, they can be used to estimate the experimental error rather than repeating each experimental condition [10]. The anodic dissolution density was selected as the response variable, because weight loss of the anode (i.e. its dissolution) would affect industrial application of the galvanic couple by compromising its physical integrity. The main variables affecting maximization/minimization of the anodic dissolution current were analyzed, and used to understand the corrosion process of the galvanic couple.

API Grade D 11B carbon steel (Table 1) was obtained from Tenaris Confab (Pindamonhangaba, Brazil).

**Table 1.** Manufacture supplied chemical composition of API Grade D 11B carbon steel.

C	Mn	P	S	Mo	Si	Ni	Cr	Cu
0.40 to 0.45	0.75 to 1.00	0.025	0.025	0.15 to 0.25	0.15 to 0.35	0.25	0.80 to 1.10	0.25

## 2.1 Shape Memory Alloy

The Laboratory of Rapid Solidification (LRS) at the Federal University of Paraiba (Brazil) provided samples of the shape-memory alloy CuAlBe (patent pending).

## 2.2 Experimental Design

The physical and chemical properties of water produced in the petroleum and gas industry was used to develop a  $2^{6-2}$  fractional design with six replicates at the central points. This experimental design was used to evaluate the effect of the following six independent variables:  $[Cl^-]$ ,  $[SO_4^{2-}]$ ,  $[S^{2-}]$ ,  $[HCO_3^-]$ , the ratio of cathodic to anodic area, and temperature on the anodic dissolution current dependent variable [10]. Statistical analysis was performed using Statistics software, version 8.0.

Corrosion in the oil industry is complex (Table 2), and this is difficult to simulate in the laboratory because it requires working with  $H_2S$  and  $CO_2$  at high pressure and temperature.

**Table 2.** Physicochemical characteristics of the water

Parameter	Well A	Well B	Well C	Well D
salinity (g/L)	38.9 ± 3.4	22.1 ± 3.3	8.4 ± 2.3	10.6 ± 3.3
chlorides (g/L)	22.67 ± 1.13	12.75 ± 1.21	5.09 ± 1.39	5.47 ± 2.18
total iron (g/L)	18.40 ± 3.96	4.46 ± 1.56	2.43 ± 2.59	0.54 ± 0.41
CO <sub>2</sub> (g/L)	**	**	**	13.0 ± 11.0
H <sub>2</sub> S (g/L)	7.25 ± 2.48	11.66 ± 2.09	25.38 ± 11.82	14.29 ± 2.97
S <sup>2-</sup> (g/L)	6.84 ± 2.35	10.95 ± 1.92	23.92 ± 11.18	13.45 ± 2.80
SO <sub>4</sub> <sup>2-</sup> (g/L)	***	100.00 *	230.00 *	25.00 *
pH	7.31 ± 0.45	7.33 ± 0.38	7.00 ± 0.54	7.68 ± 0.12
alkalinity (g/L)	781.35 ±	252.58 ± 40.81	275.39 ± 238.86	226.56 ± 85.27
Flow velocity (m.s <sup>-1</sup> )	3.9 ± 0.8	8.8 ± 0.6	0.6 ± 0.4	9.5 ± 1.2
temperature (°C)	42.5 ± 3.3	118.3 ± 8.3	74.1 ± 23.4	132.5 ± 3.5
pressure (kgf.cm <sup>-2</sup> )	12.8 ± 2.6	8.8 ± 0.6	12.7 ± 2.3	4.0 ± 0.0
Total suspended solids	44.35 *	26.38 ± 4.84	19.27 ± 0.09	21.72 ± 5.63

\* Only one measurement performed; \*\* Values changed by the content of total iron \*\*\* Not measured

Corrosion of the system (Table 3) was studied to determine how the variables influenced degradation of the material at 1 atm (1.033 kgf/cm<sup>2</sup>). The ranges of the factors were determined in accordance with the results shown in Table 2, while trying to adjust the experimental design to the minimum, maximum and medium values found in the wells to the extent possible within the laboratory conditions.

The concentration range of Cl<sup>-</sup> (mg/L) was regarded as the total salinity. Consequently, to obtain a more aggressive corroding medium, the chloride concentration in the medium was increased. The S<sup>2-</sup> concentration was defined, without considering its supersaturation by the effects of temperature and pressure. Sodium sulfide (Na<sub>2</sub>S) was used to substitute for H<sub>2</sub>S. The minimum concentration of S<sup>2-</sup> used in the experiments was 10 mg/L because it is rapidly oxidized by oxygen dissolved in the solution. In simulated aerated seawater, the concentration of S<sup>2-</sup> fell from 10 mg/L to 1.2 ± 0.2 mg/L after 1 day [11]. Bicarbonate (HCO<sub>3</sub><sup>-</sup>) was used to simulate CO<sub>2</sub>, because when it is contained in a slightly alkaline solution, it is present as H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>.

experimental limitations in the laboratory. To evaluate the effect of the CuAlBe alloy area on the dissolution of carbon steel alloy the following ratios of anodic to cathodic area (in cm<sup>2</sup>) exposed to the electrolyte were tested: 1:1; 1:0.5 and 1:0.25.

The values of the variables in the 2<sup>6-2</sup> + 6 factorial design are detailed in Table 3.

**Table 3** Values of the variables studied using the fractional factorial design 2<sup>6-2</sup> + 6 central points with the system in equilibrium with the atmosphere.

Level	-1	0	+1
Area of CuAlBe/Steel	1/4:1	1/2:1	1:1
T/°C	25	35	45
[Cl <sup>-</sup> ] ppm	8 000	24 000	40 000
[SO <sub>4</sub> <sup>2-</sup> ] ppm	10 000	15 000	20 000
[S <sup>2-</sup> ] ppm	10	20	30
[HCO <sub>3</sub> <sup>-</sup> ] ppm	40 000	50 000	60 000

### 2.3 Galvanic Corrosion

Galvanic contact between the carbon steel alloy and the CuAlBe alloy was established by forming a small circuit with the metals using a potentiostat (Model G-300, Gamry, Warminster, PA) controlled by Gamry Framework software. The potentiostat acted as a zero resistance ammeter. The tests were carried out in three electrode cells with carbon steel alloy as the primary working electrode, CuAlBe alloy as the secondary working electrode and using a coiled platinum electrode as a reference. The experiment took approximately 12 h to complete. Tests were performed immediately after preparation of the samples, which were sanded with metal sanders (400, 800, 1200, and 2000 grit) and then washed with distilled water and dried.

## 2. Results and discussion

For galvanic corrosion of Al alloy coupled with dissimilar metals, the effect of the ratio of cathodic to anodic areas ( $A_c/A_a$ ) was studied by Mansfeld et al. [12]. The rate of dissolution of an anode is directly proportional to the area of the cathode and can be calculated for any  $A_c/A_a$  ratio using Eq. (1):

$$I_d = I_g (1 + A_c/A_a) \quad (1)$$

According to Schiefler (2002) [13] this equation is only applicable to a proportion of substrates with coatings in a 1/1 ratio (coating/substrate). When there are two different alloys coupled together, the galvanic current density can be used to estimate the anodic current density. In this way the anodic dissolution current density ( $I_d$ ) can be calculated using the galvanic current density ( $I_g$ ).

Table 4 shows the matrix of the  $2^{6-2}$  design with the results for the anodic dissolution current density ( $I_d$ ). The experimental runs were randomly conducted. Depending on the experimental conditions, the anodic dissolution current density varied from 0.00 to 29.06  $\mu\text{A}/\text{cm}^2$ . The solutions were slightly alkaline, with pH values ranging from 7.63 to 8.23.



**Table 4** Fractional factorial design 2<sup>6</sup> used to study galvanic corrosion density

between carbon steel and CuAlBe alloy with the anodic dissolution current density as the dependent variable ( $I_d$ ).

Experiments	area (1)	T °C (2)	[Cl <sup>-</sup> ] (3)	[SO <sub>4</sub> <sup>2-</sup> ] (4)	[S=] (5)	[HCO <sub>3</sub> <sup>-</sup> ] (6)	pH	$I_d$ ( $\mu\text{A}/\text{cm}^2$ )	ig ( $\mu\text{A}/\text{cm}^2$ )
1	-1	-1	-1	-1	-1	-1	7.96	1.4	1.12
2	+1	-1	-1	-1	+1	-1	7.99	26.34	13.17
3	-1	+1	-1	-1	+1	+1	8.02	6.97	5.58
4	+1	+1	-1	-1	-1	+1	8.23	13.34	6.67
5	-1	-1	+1	-1	+1	+1	7.72	0.625	0.50
6	+1	-1	+1	-1	-1	+1	7.84	7.00	3.50
7	-1	+1	+1	-1	-1	-1	7.76	5.37	4.30
8	+1	+1	+1	-1	+1	-1	7.63	29.06	14.53
9	-1	-1	-1	1	-1	+1	7.85	0.14	0.11
10	1	-1	-1	1	+1	+1	7.77	8.84	4.42
11	-1	1	-1	1	+1	-1	7.60	2.96	2.37
12	1	1	-1	1	-1	-1	7.80	9.5	4.75
13	-1	-1	1	1	+1	-1	7.72	1.23	0.98
14	1	-1	1	1	+1	-1	7.70	10.28	5.14
15	-1	1	1	1	-1	+1	7.67	0.38	0.30
16	1	1	1	1	+1	+1	7.60	0.0	0.0
17	0	0	0	0	0	0	7.84	8.62	5.75
18	0	0	0	0	0	0	7.80	13.8	9.2
19	0	0	0	0	0	0	7.86	11.55	7.7
20	0	0	0	0	0	0	7.83	17.20	11.47
21	0	0	0	0	0	0	7.85	16.8	11.20
22	0	0	0	0	0	0	7.80	12.21	8.14

In the galvanic current density results (Table 4), the largest increase in the response variable was observed for when the area of cathodic to anodic. This indicates the area ratio is the main factor affecting corrosion of the galvanic couple. The magnitude of increase because of this effect was even greater when the anodic dissolution current density of the carbon steel ( $I_d$ ) was taken into consideration, because it increased the number of electrons per second produced in the anode. Because of this, the estimated values of  $I_d$  moved from higher values than the current statistical model



proposed. This confirms the effect of area on the middle and validates the results, as was observed in the response surfaces for the area.

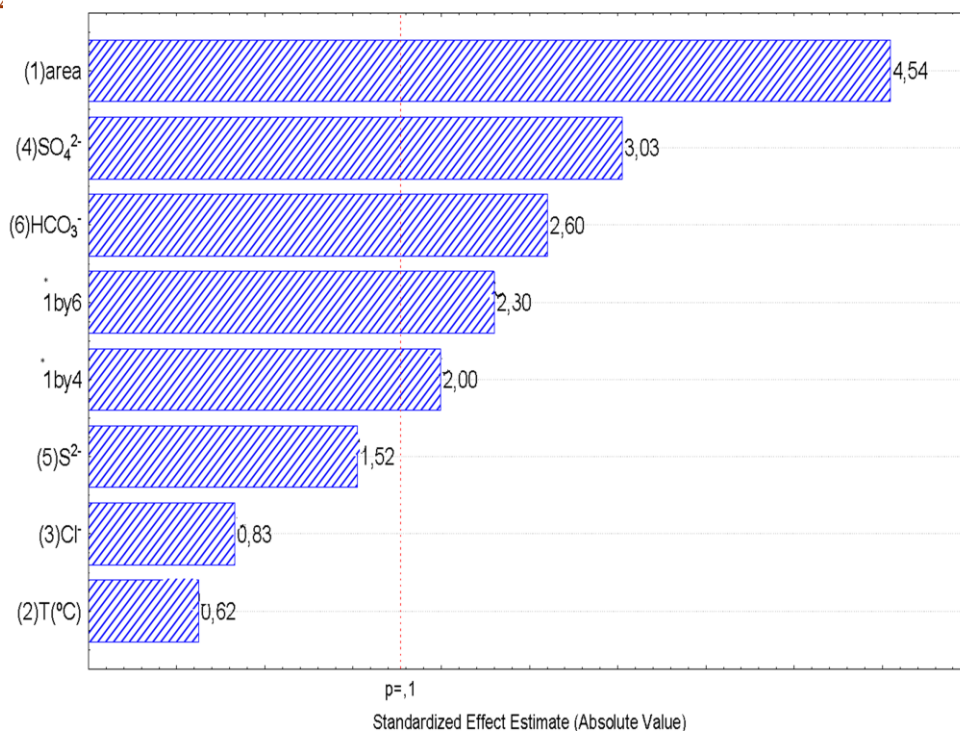
To verify the experimental results, variables that affected the response of the dependent variable were estimated. This variation is called experimental error and it is a statistical error arising from uncontrollable test conditions. In this study, the level of significance level was defined as  $p=0.10$ . Among the variables studied, only the  $A_c/A_a$  ratio and the concentrations of  $[SO_4^{2-}]$  and  $[HCO_3^-]$  were statistically significant (Table 5).

**Table 5** Effects of the independent variables on the dependent variable.

Variable	Effect	Standard Error	p-value
Average	9.25	1.22	<0.001
Area	10.66	2.56	0.002
Temperature (°C)	1.46	2.86	0.6150
$[Cl^-]$	-1.94	2.86	0.507
$[SO_4^{2-}]$	-7.10	2.86	0.025
$[S^{2-}]$	3.58	2.86	0.230
$[HCO_3^-]$	-6.10	2.86	0.050

Data obtained for a statistical study with a 90% rate of accuracy.

Figure 1 shows a Pareto chart for the results. All the effects that go beyond the 0.10 line are significant. This graph confirms that  $[S^{2-}]$ ,  $[Cl^-]$ , and the temperature did not significantly affect dissolution of the anode. The fractional factorial design can be used to define the variables of that influence the response variable, and to study their effects on the current anodic dissolution. When the effect of one variable depends on the level of the other variables, first-order interaction occurs between the variables. First-order interactions (e.g. area and  $HCO_3^-$ , area and  $SO_4^{2-}$ ) can be confused between themselves, difficult to distinguish.



**Figure 1** Pareto diagram for analyzing the effects of independent variables on the anodic dissolution current.

Temperature is an important variable because it increases electrolyte conductivity and transport of ions, acceleration of electrochemical reactions at the electrode/electrolyte interface, decreases polarization, and increases solubilization of protective films [7]. However, in the studied range, the effect of this variable was not significant (Figure 1).

Cruz et al. studied the effect of the temperature of the electrolytic medium on the galvanic current density intensity (response variable) in chloride ions [9]. A complex situation of passivation and despassivation was observed, in which the film was both protective and destroyed. Therefore, a more complex electrolyte is necessary to use a statistical approach as interaction among different variables may increase or reduce the effects of the other variables.

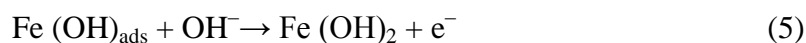
Dissolution of iron present in the carbon steel occurs in accordance with Eq. (2):



Iron oxidation in an alkaline solution occurs in two main stages, the first of which follows Eq.(3):



The reaction occurs in two partial steps (Eqs. 4 and 5), along with the adsorption of  $\text{OH}^-$  ions [14].



Formation of  $\text{Fe}(\text{OH})_2$  is subject to the formation of an intermediate product ( $\text{HFeO}_2^-$ ) [15].

When the anodic dissolution density is analyzed, it is important to consider that passivation of the anodic surface can diminish or even completely stop dissolution of the anode. Depending on the solution, the passive film on the surface of carbon steel can be composed of an oxide, hydroxides, or basic salts such as carbonates and sulfates. In this way, the negative effect in Table 5 can indicate formation of a protective film. It should be noted that negative values for the effects of the independent variables on the dependent variable indicate negative effects on the anodic dissolution current density, that is increases in the ion concentration decrease the values of the response variable. This is particularly true when, as a result of highly concentrated solutions, the solubility limit is exceeded and a film forms on the surface of the anode through precipitation. However, the type of precipitated film was not determined in the present study.

The electrons on the surface of the CuAlBe alloy interact with a complex system composed of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{HO}^-$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$ . Therefore, the possible cathodic reactions (Eqs. 6 and 7) are as follows:



These equations describe the types of electrochemical activity, but there is a possibility of reaction between copper metal and oxygen molecules:

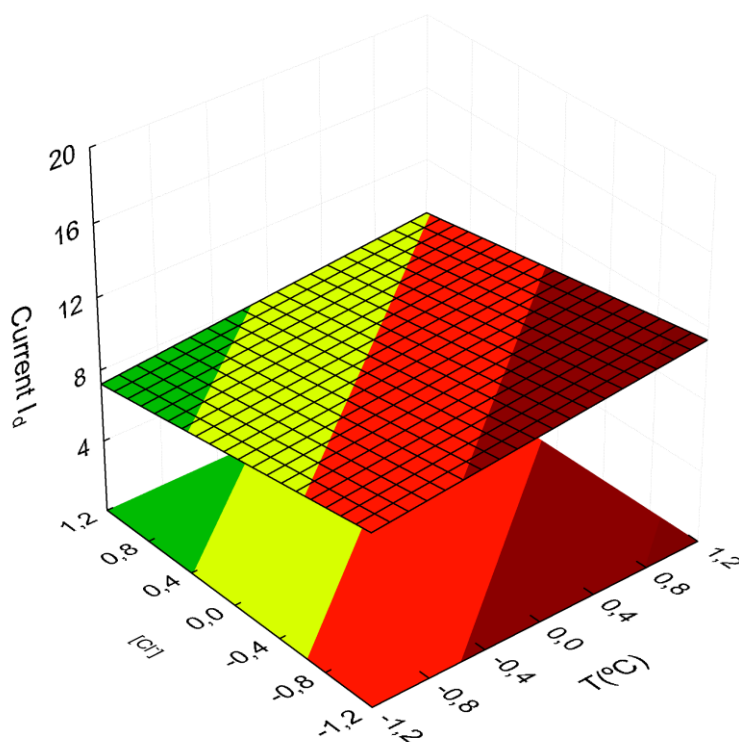


These hypotheses were raised because of a visual inspection, in which formation of a dark film was observed on the surface of the cathode. This film was probably cuprite and/or tenorite. It is known that, depending on the nature of the corrosive medium, the cathodic reaction may involve absorption of oxygen, but deposition of films has also been observed.

$I_g$  is associated with the concepts of thermodynamics and chemical kinetics. The thermodynamic process of galvanic corrosion is spontaneous, and  $\Delta G$  is negative. This implies that corrosion will occur naturally without an external potential. Electroneutrality dictates that, for a galvanic couple, the dissolution rate of the anode must be equal to the rate of the reduction reaction on the cathode. However, in the present case there would be passive film formation, chemical reactions and ionic interference in the medium. In this manner,  $I_g$  was analyzed also taking into account film formation, which tends to minimize the response variable. Physically, when studying  $I_g$  one must understand that it is associated with both anodic and cathodic current densities. The generated response surfaces with  $I_d$  as the response variable can

be contrasted with the response surface generated from  $I_g$  [9]. Trends observed are caused by the cathodic current density (i.e. changes in the cathode).

Cruz et al. analyzed the response surface for  $I_g/T/[Cl^-]$  dependence [9]. Comparison with that obtained in this study for  $I_d/T/[Cl^-]$  (Figure 2), indicates that some event occurs in the cathodic region that contributes to the quasi-suppression of the galvanic current density. It is hypothesized that chloride ions accelerate precipitation of a protective film on the cathode. This implies that the anodic dissolution can be affected by formation of this film on the cathode, hindering galvanic corrosion.

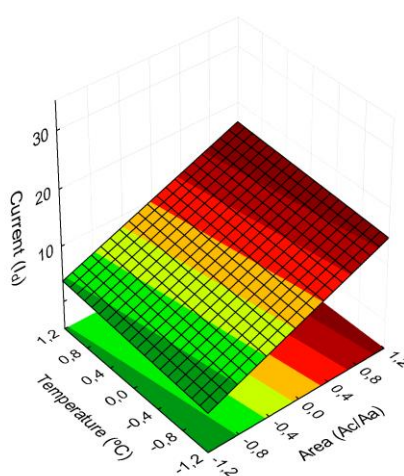


**Figure 2** Response surfaces as a function of temperature and  $[Cl^-]$ .

The use of experimental design is important for understanding of the corrosion process. With this set of experiments it is possible to assess several response variables for an electrochemically complex medium. In this way, equations that are representative

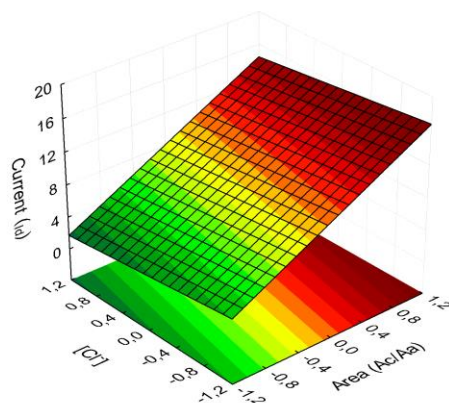
of the process can be proposed, demystifying the concept that experimental design only proposes equations without physical meaning.

Figure 3 shows the response surfaces for the anodic to cathodic area and the other variables. The anodic to cathodic area showed a positive effect on the anodic dissolution current density, indicating that increasing cathodic area increased dissolution of the anode (Figure 3 a–e). The ratio between the areas is unfavorable when the surface of the more noble metal is larger than that of the more active member, in which case accelerated dissolution of the anode is predicted. This result has been discussed extensively in the literature [16-18]. However, the use of a complex electrolyte is what sets this study apart.

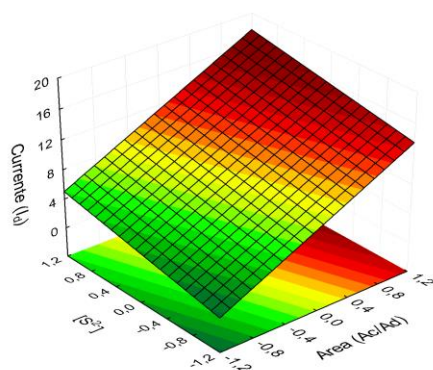


a)



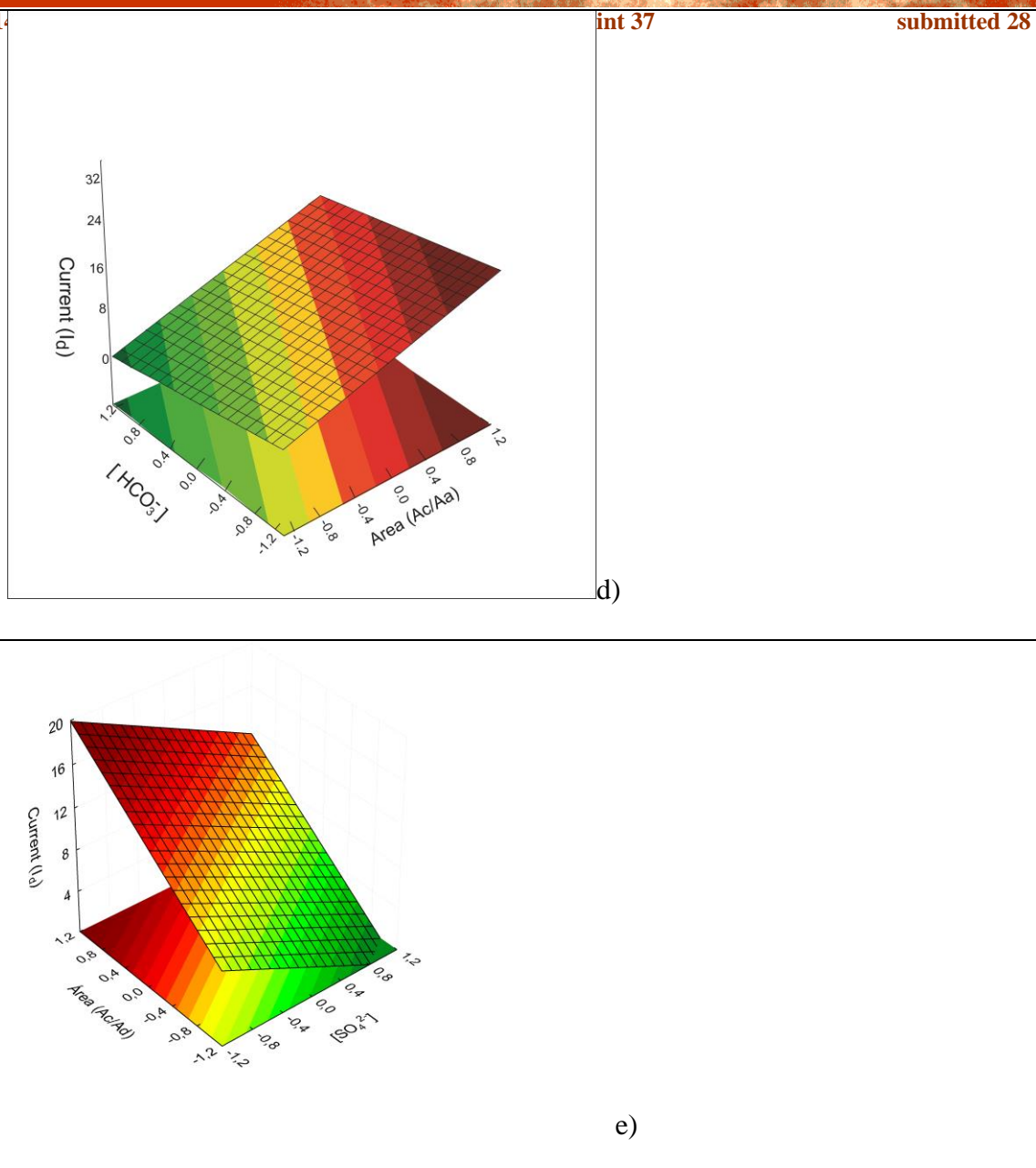


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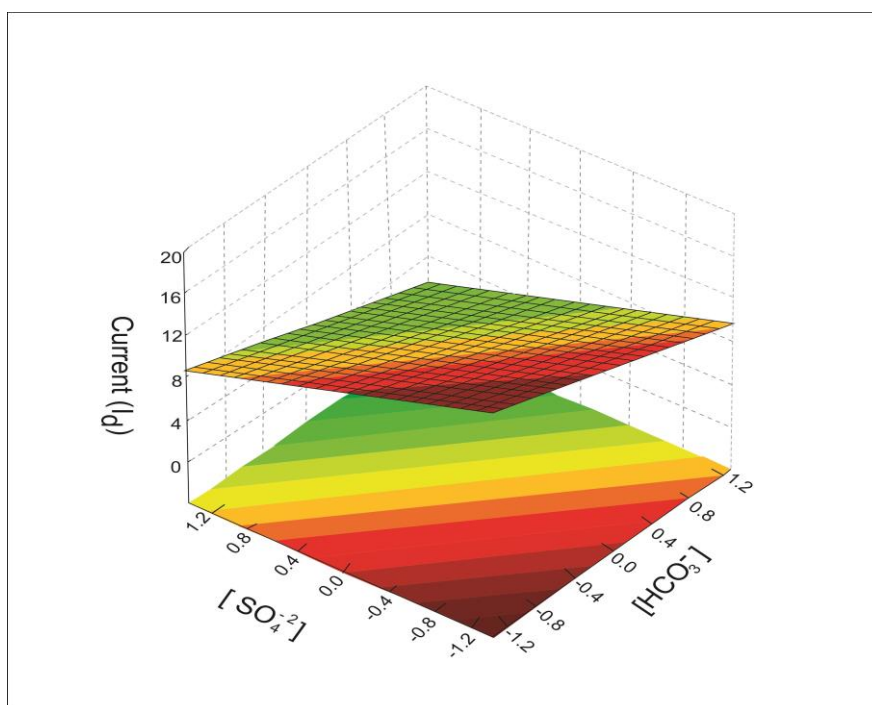




**Figure 3** Response surfaces as a function of a) area and temperature; b) area and  $[Cl^-]$ ; c) area and  $[S^{2-}]$ ; and d) area and concentration of  $[HCO_3^-]$  e) area and  $[SO_4^{2-}]$ .

Increases in  $[HCO_3^-]$  (Figure 2 d) and  $[SO_4^{2-}]$  showed a negative effect on the anode dissolution density.

Figure 4 shows that within the range studied,  $[SO_4^{2-}]$  and  $[HCO_3^-]$  have synergistic effects on anode dissolution.



**Figure 4** Response surfaces according to  $[\text{SO}_4^{2-}]$  and  $[\text{HCO}_3^-]$ .

Carbonate and sulfate ions present potentiating effects, because they enhance the anodic dissolution current when their concentrations in the electrolyte solution decrease. This indicates that the protective films are not formed under these conditions and that dissolution of the anode is maximized.

### 3. Conclusion

The best conditions for minimizing the dissolution current of the anode were determined. A lower anodic current density was found when the cathode area as minimized compared to the anodic area. Furthermore, an analysis of the response surfaces showed that  $[\text{SO}_4^{2-}]$  and  $[\text{HCO}_3^-]$ , and the  $\text{SO}_4^{2-} - \text{HCO}_3^-$  interaction significantly influenced the anodic dissolution current. An interesting fact, was the analysis of the response surface for  $I_g/T/[\text{Cl}^-]$  comparing with that obtained in this study for  $I_d/T/[\text{Cl}^-]$ , indicates that some event occurs in the cathodic region that contributes to

the quasi-suppression of the galvanic current density. Moreover, anodic and/or cathodic passivation could suppress dissolution of the metals and an experimental design can be used to understand the physical process of its dissolution. Anodic dissolution is a complex process that can result in overlapping of a number of phenomena.

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