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OPTIMIZATION OF THE INHIBITION EFFECT OF SODIUM PHOSPHATE ON THE CORROSION OF ORDINARY STEEL IN SEA WATER BY EXPERIMENTAL DESIGN

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ABSTRACT

In this work, we have studied the influence of three parameters on the corrosion rate of ordinary steel in marine environment of the Atlantic Ocean, because the study of each parameter independently cannot predict the best conditions to obtain a minimum corrosion rate. To overcome this problem, we chose a three-factor Doelhert matrix as the experimental model. The response (corrosion rate) was evaluated by the gravimetric method. We chose the most used parameters in the field of corrosion such as inhibitors concentration, immersion time and pH of the medium. This approach allowed us to find the best conditions for obtaining a minimum corrosion rate.

Keywords: *steel, seawater, weight loss, corrosion, experimental design.*

INTRODUCTION

Year after year, the cost of marine corrosion has increased to 4 % of each country's Gross Domestic Product (GDP) today. An informed approach to material selection, protection and corrosion control is needed to reduce the burden of wasted materials, wasted energy and wasted money. These notes were compiled by marine corrosion researchers to help designers, engineers and marine equipment users understand the causes of marine corrosion and use protection systems and materials that are more resistant to marine corrosion [1 - 3].

Steel has been widely used as tubing material for condensers and heat exchangers in various cooling water systems because of their resistance to corrosion. Steel materials are extensively used to fabricate structures and components exposed to sea water and other marine environments [4 - 6]. Among the methods used to protect materials and more specifically steel we mention the use of non-toxic inhibitors. The use of inorganic phosphate inhibitors is mainly justified by its non-toxicity. The literature indicates that the addition of phosphate ions to the chlorine solution significantly reduces the rate of corrosion by promoting the formation of a phosphate-rich passive layer on the surface of the steel. This layer acts as a physical barrier against the diffusion of chloride ions [7 - 10].

The current work is a contribution to the study of the optimization of inhibition of steel corrosion in an environment where seawater is found. The main interest was in determining the influence of sodium phosphate concentration and temperature and pH on the rate of corrosion of steel in seawater. The influence of these factors was tested using the experimental model methodology [11].

The model 2k (K factors with 2 levels each one) is most widespread because being the least prohibitory at the financial level while remaining powerful. Among the advantages of the experimental designs are: reduction amongst tests, detection of the interactions between factors, modeling of the studied answer and an optimum precision of the results.

EXPERIMENTAL

Material

The weight loss tests are of a simple implementation, the apparatus necessary to perform these mass loss measurements involves:

- An analytical balance (accurate to four digits after the decimal point).
- A pH meter that is used to indicate the pH and temperature of the tested solution.
- A Haier brand thermostat keeps the electrolyte at a constant temperature 25 ± 0.2°C.
- Glass bottle of 100 mL.

Specimens

Ordinary steel specimens containing 0.11 % C, 0.24 % Si, 0.47 % Mn, 0.12 % Cr, 0.02 % Mo, 0.1 % Ni, 0.03 % Al, Co < 0.0012 %, Cu 0.14 %, V < 0.003 % , W 0.06 % and the remainder Fe was used as the substrate. These steel specimens were mechanically cut into 1cm × 5 cm × 0.06 cm dimensions for weight loss experiment. Prior to all measurements, the specimens were mechanically polished on wet SiC paper (grade 400 - 600 - 1200), rinsed with doubly distilled water, degreased ultrasonically in ethanol for 5 min and dried with hot air.

Electrolytes

The electrolyte used in this study is saline seawater 35g/L, the average chemical composition of which is given in the table below:

Table 1. The chemical composition of sea water.

Substances	Content (g/L)
Sodium chloride	27.20
Magnesium chloride	3.80
Magnesium sulphate	1.65
Calcium sulphate	1.26
Potassium sulphate	0.86
Calcium carbonate	0.12
Magnesium bromide	0.076
Other substances	Content (mg/L)
Fluorine	1.40
Silica	1.00
Nitrogen	1.00
Phosphor	0.060
Barium	0.055
Iron	0.050
Iodine	0.050

Gravimetric measurement

The weight loss method is a simple implementation and does not require important equipment. The corrosion rate is determined after 72 hours immersion.

The corrosion rate is calculated by the following formula:

$V = \Delta m / S.t$

where $\Delta m = M_1 - M_2$ represents the difference between the initial mass M_1 and the final mass M_2. S is the surface of the metal exposed to the solution.

The strategy of the experimental design

Our interest is to minimize the rate of corrosion. This represents the response of the experimental design. To achieve this aim we determined the high and low levels of the chosen factors such as inhibitor concentration, temperature and pH. The brainstorming indicates the values given in Table 2.

Table 2. The high and low levels of factors.

Factor	Low level	High level
Concentration	10^{-5}M	10^{-3} M
Temperature	20°C	40°C
pH	7	10

Table 3. The possible combinations with the signs.

Combination	Concentration	Temperature	Time
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+

"+" Indicates high levels (e.g. 10^{-3}M for concentration or 40°C for temperature) and "-" indicates low levels (7 for pH). After the determination of the signs + and - we replace them by their values.

Table 4. The combinations with the values of the factors.

Combination	Concentration	Temperature	pH
1	10^{-5} M	20°C	7
2	10^{-3}M	20°C	7
3	10^{-5} M	40°C	7
4	10^{-3}M	40°C	7
5	10^{-5} M	20°C	10
6	10^{-3}M	20°C	10
7	10^{-5} M	40°C	10
8	10^{-3}M	40°C	10

The construction of the experimental plan has been realized by permutation of the signs without using a specific software, the possible combinations are shown in Table 3. There are eight possibilities.

"+" Indicates high levels (e.g. 10^{-3}M for concentration or 40°C for temperature) and "-" indicates low levels (7 for pH). After the determination of the signs + and - we replace them by their values.

RESULTS AND DISCUSSION

Response

For experiment 1, we will determine the level of the corrosion rate with a concentration of 10^{-5} M, a temperature of 20°C and pH of 7. For experiment 2, we will take a concentration of 10^{-3} M, a temperature of 20°C and pH of 7, etc. The results obtained are given in Table 5.

Analysis of the results

We will carry out 7 analyzes:

- Analysis of the impact concentration;
- Analysis of the impact temperature;
- Analysis of the impact pH;
- Analysis of the impact concentration and temperature;
- Analysis of the impact temperature and pH;
- Analysis of the impact concentration and pH;
- Analysis of the impact concentration, temperature and pH.

To perform these analyzes, we will perform some simple calculations. The effect of each factor on our response (corrosion rate) can be measured as follows: The sum of the high-level responses divided by 4 (since 4 "+" was used) minus the sum of the low-level responses divided by 4 (since 4 "-" were used).

$$\frac{(4.87 + 5.20 + 3.44 + 4.25)}{4} - \frac{(7.89 + 8.16 + 6.50 + 6.66)}{4} = -2.86$$

It can be concluded that the response which is the rate of corrosion decreases by 2.86 when the concentration takes its high value (10^{-3} M).

Analysis of the temperature factor gives:

$$\frac{(8.16 + 5.2 + 6.66 + 4.25)}{4} - \frac{(7.89 + 4.87 + 6.50 + 3.44)}{4} = 0.39$$

When the temperature reaches its high value (40°C) the corrosion rate increases by 0.39.

Table 5. The combinations with response.

Combination	Concentration	Temperature	pH	Corrosion rate (mg/h.cm^2)
1	10^{-5} M	20°C	7	7.89
2	10^{-3}M	20°C	7	4.87
3	10^{-5} M	40°C	7	8.16
4	10^{-3}M	40°C	7	5.20
5	10^{-5} M	20°C	10	6.50
6	10^{-3}M	20°C	10	3.44
7	10^{-5} M	40°C	10	6.66
8	10^{-3}M	40°C	10	4.25

Analysis of the pH factor gives:

$$\frac{(6.50+3.44+6.66+4.25)}{4}-\frac{(7.89+4.87+8.16+5.20)}{4}=-1.32$$

When pH takes its high value (10) the corrosion rate decreases by 1.32.

The pH factor has a very important impact on the response as the temperature factor but is lower than the concentration.

For reasons of space, we have called concentration factor A, temperature factor B and pH factor C. AxB is therefore the combination of concentration - temperature, BxC is temperature - pH, AxC is concentration-pH, AxBxC is concentration - temperature - pH. The results of each combination are simply the mathematical results of the mixture of factors.

Thus, for AxB, the combination of concentration and temperature, the first combination gives "-" for the concentration and "-" for the temperature. The result AxB is "-" x "-" which gives us a "+", etc.

Analysis of the AxB combination:

$$\frac{(7.89+5.20+6.50+4.25)}{4}-\frac{(4.87+8.16+3.44+6.66)}{4}=0.18$$

Analysis of the BxC combination:

$$\frac{(7.89+4.87+6.66+4.25)}{4}-\frac{(8.16+5.20+6.50+3.44)}{4}=0.09$$

Analysis of the AxC combination:

$$\frac{(7.89+8.16+3.44+4.25)}{4}-\frac{(4.87+5.20+6.50+6.66)}{4}=0.13$$

Analysis of the AxBxC combination:

$$\frac{(4.87+8.16+6.50+4.25)}{4}-\frac{(7.89+5.20+3.44+6.66)}{4}=0.15$$

The increasing order according to the importance of the effect of the combinations is as follows:

$$\mathrm{BxC} < \mathrm{AxC} < \mathrm{AxBxC} < \mathrm{AxB}$$

Table 6. The combinations of the interactions between factors with the values of the factors.

Combination	Concentration	Temperature	pH	AxB	BxC	AxC	AxBxC	Corrosion rate (mg/h.cm^2)
1	10^{-5} M	20°C	7	+	+	+	-	7.89
2	10^{-3} M	20°C	7	-	+	-	+	4.87
3	10^{-5} M	40°C	7	-	-	+	+	8.16
4	10^{-3} M	40°C	7	+	-	-	-	5.20
5	10^{-5} M	20°C	10	+	-	-	+	6.50
6	10^{-3} M	20°C	10	-	-	+	-	3.44
7	10^{-5} M	40°C	10	-	+	-	-	6.66
8	10^{-3} M	40°C	10	+	+	+	+	4.25

Table 7. The effects of the combinations.

Factor	effect
A	−2.86
B	0.39
C	−1.32
AxB	0.18
BxC	0.09
AxC	0.13
AxBxC	0.15

The chosen model

The complete model, with the main effects and the interactions is:

$$Y = b0 + b1X1 + b2X2 + b3X3 + b12X1X2 +$$

$$+b23X2X3 + b13X1X3 + b123X1X2X3$$

In terms of calculations, we obtain for example:

$$b0 = \frac{(7.89 + 4.87 + 8.16 + 5.20 + 6.50 + 3.44 + 6.66 + 4.25)}{8} = 5.22$$

$$b1 = \frac{\text{Impact de A}}{2} = \frac{-2{,}86}{2} = -1.43$$

$$b12 = \frac{\text{Impact de A} \times \text{B}}{2} = \frac{0.18}{2} = 0.9$$

The mathematical model of the experimental plan written after the calculation of the coefficients is:

$$Y = 5.22 - 1.43X1 + 0.1952X2 -$$
$$+ 0.075X1X2X3$$

$$0.66X3 + 0.9X1X2 + 0.045X2X3 + 0.065X1X3$$

With the full model we estimated 8 coefficients ($p = 8$) using 8 experiments ($n = 8$). It is not possible in this case to estimate the variance s^2 of the random variable e, so it is not possible to give a confidence interval for the coefficients of the model.

According to the results obtained we can notice that the concentration is the most influencing factor on the rate of corrosion followed by the pH factor, the two factors decrease the response when take its high value, the literature shows that the concentration of the inhibitor increases the inhibitory efficiency and decreases the rate of corrosion because the phosphate ions intervene directly to inhibit anodic corrosion reactions and promote the formation of protective layers by means of mixed compounds insoluble with iron ions [7 - 8].

When the pH is high the rate of corrosion is decreasing. This behavior has been explained by the fact that the presence of hydroxide ions favors the ionic form of PO_4^{3-} [12]. The ionic form combines with Fe^{+2} to give the chelate. These results are in very good agreement with those obtained by Touir et al. [13].

CONCLUSIONS

It will be essential to control the concentration and the pH (for example, by applying a maximum concen-

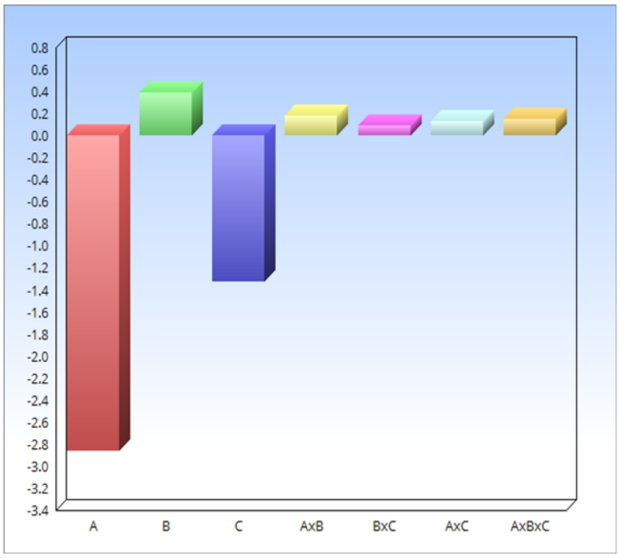

Fig. 1. Linear histogram for the effect of each combination.

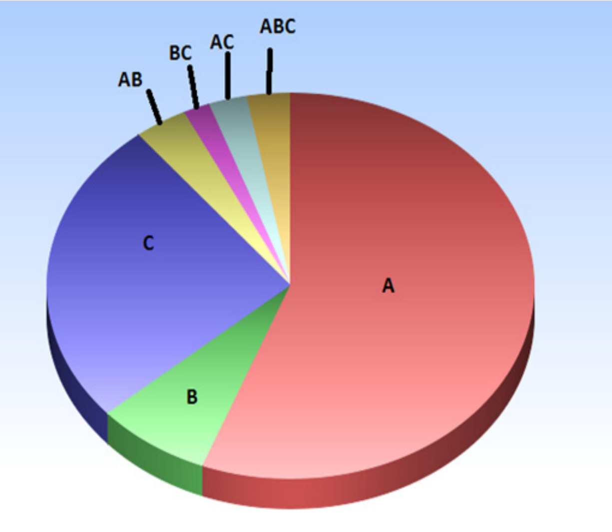

Fig. 2. Circular histogram of the effect of each combination.

tration 10^{-3} M, and maximum pH 10 without taking into account the other parameters) in order to optimize the rate of corrosion.

The response methodology was used to search for the best conditions using sodium phosphate as a corrosion inhibitor for steel in seawater. The strategy of the experimental plans we followed will allow us to find the best conditions for obtaining the minimum corrosion rate.

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