

Application of response surface methodology method in designing corrosion inhibitor

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Abstract. In oil and gas pipelines and offshore structure, inhibitors have been considered to be the first choice to reduce corrosion rate. There are many corrosion inhibitor compositions available in the market. To produce the best corrosion inhibitor requires many experimental data which is not efficient. These experiments used response surface methodology (RSM) to select corrosion inhibitor compositions. The experiments investigated effects of corrosion inhibition on corrosion rate of low carbon steel in 3% NaCl solution with different concentrations of selected main inhibitor compositions which are ethyl acetate (EA), ethylene glycol (EG) and sodium benzoate (SB). Corrosion rate were calculated using linear polarization resistance (LPR). All of the experiments were set in natural conditions at pH 7. MINITAB[®] version 15 was used for data analysis. It is shown that a quadratic model is a representative model can predict best corrosion inhibitor composition comprehensibly.

1. Introduction

Corrosion is the destructive attack of materials through reaction with its environment. Corrosion is an important and critical issue faced in various industrial sectors [1-3]. The offshore structures, which always exposed to NaCl solutions, rain, condensation, and water, constantly exposed to severe corrosion. One method for controlling the metal losses that occurs due to corrosion in pipelines is to use a corrosion inhibitor.

Corrosion inhibitors are chemical substances or mixtures which are added in low concentrations to an aggressive environment for reducing corrosion rate of a material [4]. Typically they work by adsorbing themselves on the metal surface, and form film on it to protect the surfaces of metal. Among various methods to prevent the destruction or degradation of metal surface, corrosion inhibitor is the best methods of corrosion protection due to its low cost and practical method.

According to National Association of Corrosion Engineers (NACE) [5-7], inhibitors can be classified into anodic, cathodic or mixed depends on the intervention by the reaction of corrosion inhibitor preferentially in the anodic or cathodic sites or engage in both sites. They are widely used to minimize or reduce the rate of corrosion of metal structures.

The common inhibitors that were being used are nitrates, benzoates, phosphates, and chromates. Since it is almost impossible to prevent corrosion, it is more apparent that controlling the rate of corrosion can be the most economical solution. Hence, this study is set to design a novel corrosion inhibitor of selected chemicals which are ethyl acetate, ethylene glycol, and sodium benzoate for corrosion protection on offshore structure that will be useful for oil and gas industry in future. The main objective of this research is to design a novel inhibitor with optimum corrosion performance that



can be used as a corrosion protection in oil and gas environments. (RSM) methods have become a feasible tool to simplify empirical corrosion models [8-10].

2. Research methodology

2.1. Modelling work

Experimental design for corrosion using central composite design (CCD) is an accepted experimental approach in RSM. It enables the construction of a second order (quadratic) model without the need to perform a full factorial design experiment. Using response information, the optimum data between factors can be developed, and model improvements can be achieved. The application of RSM with a CCD technique suggests a design model to calculate the response variables at specific environmental values [11,12].

Table 1. Relationship between natural and coded variable levels of dependent variables used in RSM to study effects of components to select inhibitor.

Level	Code	Concentration of Inhibitor		
		Ethyl Acetate (A) (ppm)	Ethylene Glycol (B) (%)	Sodium Benzoate (C) (ppm)
Axial point	1.7	500	50	500
High	1	400	40	400
Centre	0	300	30	300
Low	-1	200	20	200
Axial point	-1.7	100	10	100

2.2. Electrochemical Set-up

A typical schematic three-electrode set-up used in all electrochemical experiments is shown in Figure 1. A low carbon steel was used as the working electrode. Glass cell was fitted with graphite electrodes as auxiliary electrode and Ag/AgCl as a reference electrode [13].

2.3. Specimen Preparation

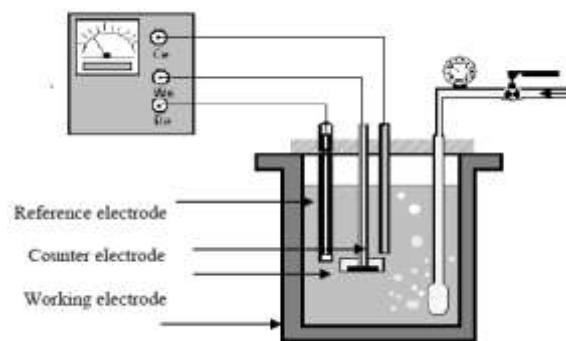
The working electrodes were carbon steels. The cylindrical specimens have diameter of 12 mm and 10 mm thickness. Before immersion, the specimen surfaces were polished successively with 240, 400 and 600 grit SiC paper, rinsed with methanol and degreased using acetone. The experiments were repeated at least twice in order to ensure reasonable reproducibility.

2.4. Cell Solutions

The experiments were performed both in stagnant solutions condition. The test pressure was 1 bar, the glass cell was filled with 1 liter of distilled water and 3% wt NaCl which was stirred with magnetic stirrer. Temperature was set using a hot plate. The Linear Polarization Resistance (LPR) technique was used to measure the corrosion rate. The procedure is similar to ASTM Experimental test G 5-94 [14].

Table 2. Central-composite experimental design of the independent variables with the observed values for the response, (Y_i).

CODE			NATURAL		
A	B	C	A (ppm)	B (%)	C (ppm)
0	-1.7	0	300	10	300
0	0	0	300	30	300
0	0	-1.7	300	30	100
-1	-1	1	200	20	400
1	1	-1	400	40	200
-1.7	0	0	100	30	300
1.7	0	0	500	30	300
0	0	0	300	30	300
1	-1	-1	400	20	200
0	0	0	300	30	300
0	0	0	300	30	300
1	-1	1	400	20	400
-1	1	1	200	40	400
0	1.7	0	300	50	300
0	0	1.7	300	30	500
-1	-1	-1	200	20	200
-1	1	-1	200	40	200
0	0	0	300	30	300
1	1	1	400	40	400
0	0	0	300	30	300

**Figure 1.** Schematic of corrosion test cell.

3. Results and discussion

3.1. Fitting corrosion predictions model at pH 5.5

Corrosion predictions model at pH 7 was fitted using second-order polynomial pattern. The model proposed for the response is given below. The model was calculated using Minitab software program [15].

$$\begin{aligned} \text{Corrosion Rate} = & 0.122 - 0.000220 \text{ EA} - 0.00141 \text{ EG} - 0.000156 \text{ SB} + 0.000017 \text{ EG}^2 \\ & + 0.000001 \text{ EA} * \text{EG} + 0.000001 \text{ EG} * \text{SB} \end{aligned} \quad (1)$$

Where:

EA: Ethyl Acetate

EG: Ethylene Glycol

SB: Sodium Benzoate

For linear relationship, EA shows the most effect in reducing the corrosion rate followed by SB and EG respectively. On the other hand, for square relationship, SB*SB shows the lowest value of corrosion rate, then followed by EG*EG and EA*EA respectively. For two way interaction, EG*SB indicates the most effect in reduce the corrosion rate, and then followed by EA*EG and EA*EA.

3.2. Analysis and interpretation of response surface design

In order to examine how the factors influence the response, the factorial plots were done by plotting the data means or also known as fitted means. Figure 2 below shows the main effects plot for corrosion rate.

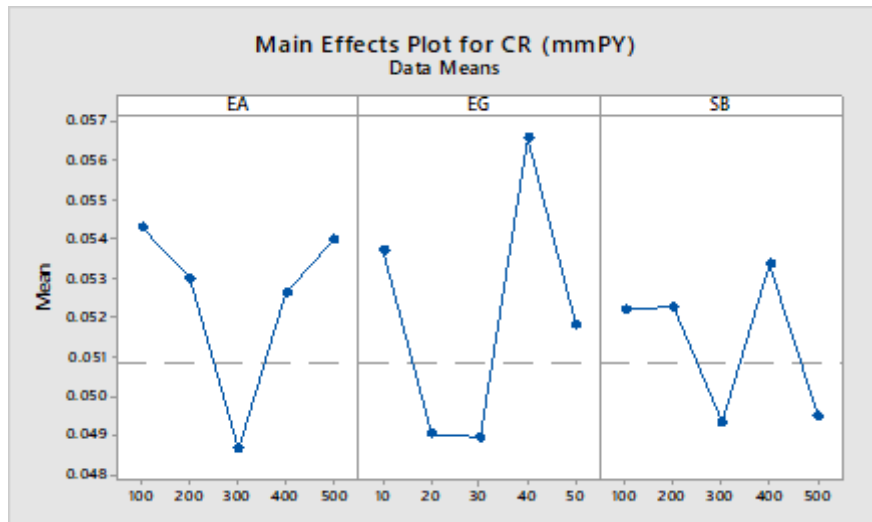


Figure 2. Main effects plot for corrosion rate.

Figure 2 shows the main effects plot of corrosion rate for low carbon steel in NaCl with different concentration of inhibitors. For ethyl acetate, when the concentration decrease from 100 to 300 ppm, the corrosion rate decreases until it reaches a minimum value of 0.0485 mmPY, then increased with increasing concentrations from 300 to 500 ppm. As for ethylene glycol, the minimum value of corrosion rate is at 30 % in water with 0.0489 mmPY and the maximum value is at 40 % in water with 0.0565 mmPY. For sodium benzoate, the minimum corrosion rate is at 300 ppm with 0.0492 mmPY and the maximum is at 400 ppm with 0.0531 mmPY.

The contour plots with 2D contour lines were done by plotting the relationship between two continuous predictors and a fitted response. They were produced for all pairs of continuous variables in separate panels on the same graph for corrosion rate and Icorr. Due to synergistic effect of these mixed inhibitor, the simultaneous combined effects of the concentration with different types of inhibitor on the corrosion rate and Icorr are shown in Figure 3.

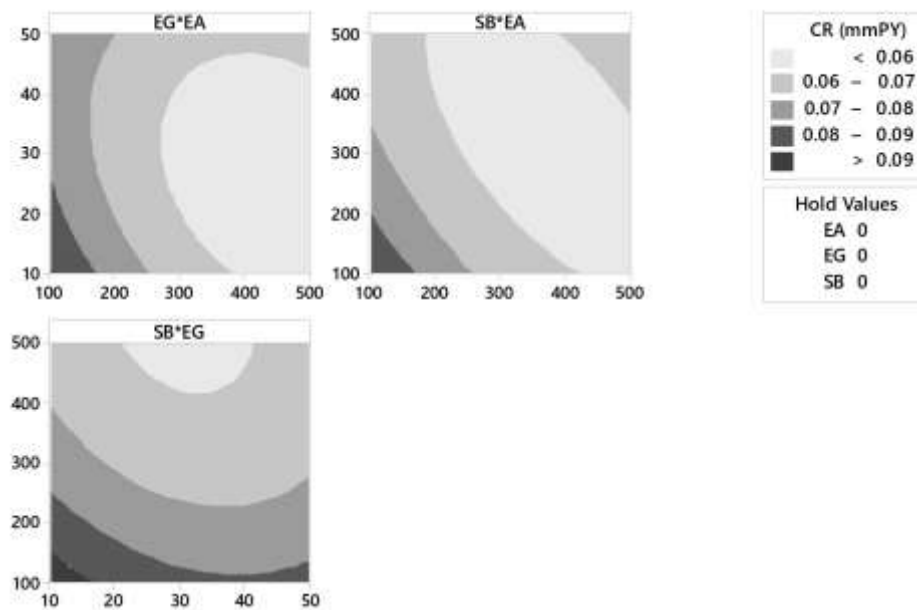


Figure 3. Contour plots of corrosion rate.

As illustrated in Figure 3, the contour plot of ethyl acetate and ethylene glycol indicates that the greatest corrosion rate is about 100 ppm of ethyl acetate with around 20 to 30 % in water of ethylene glycol, and the area appears at the bottom left of the plot. The smallest corrosion rate is when the concentration of ethyl acetate is about 480 ppm with about 20 to 30 % in water of ethylene glycol which appears at the centre of the plot. Besides, from the contour plot of ethyl acetate and sodium benzoate, the greatest corrosion rate takes place with 100 ppm for both sodium benzoate and ethyl acetate, which appears at the lower left of the plot. The smallest corrosion rate for these chemical is when the concentration of both of them around 300 to 400 ppm which located at the centre of the plot. Next, from the contour plot of sodium benzoate and ethylene glycol, it shows that the greatest corrosion rate is at 100 ppm of sodium benzoate and around 10 % in water of ethylene glycol where it appears at the lower left of the plot, while the smallest corrosion rate is when the concentration of sodium benzoate is around 420 to 500 ppm, with around 30 % of ethylene glycol in water.

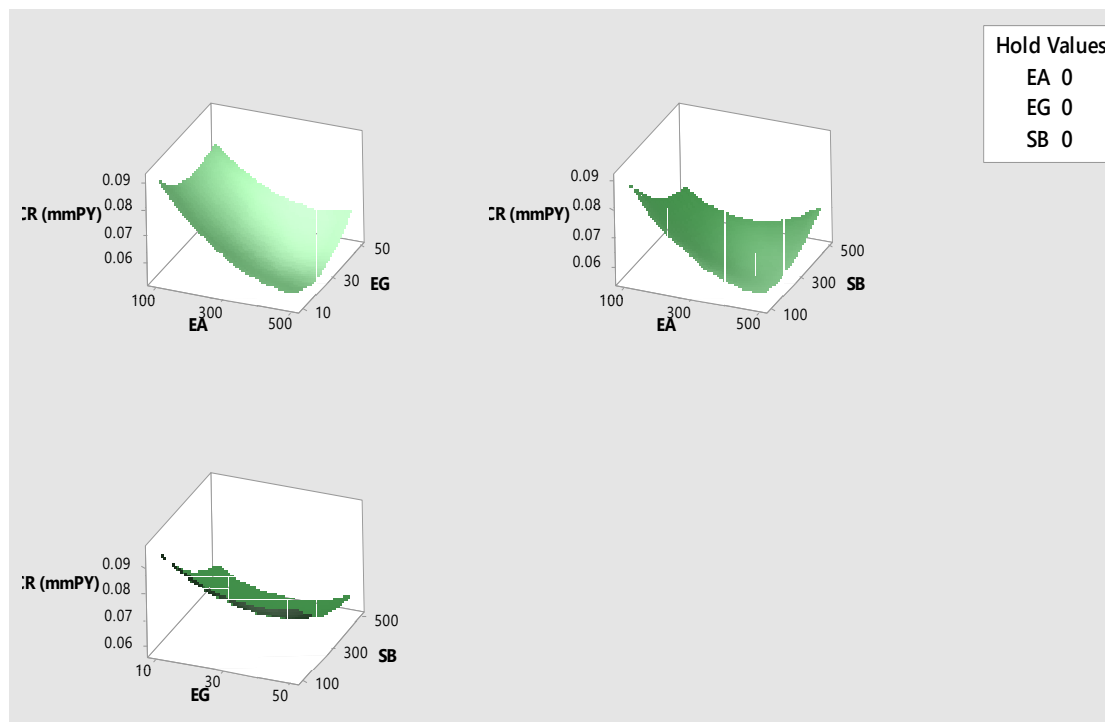


Figure 4. Surface plots of corrosion rate [15].

Figure 4 shows the results of three dimensional view that provides a clear vision of corrosion rate. From the figure, it is clearly shown that the area represent for the lowest corrosion rate of the surface plot of ethyl acetate and ethylene glycol is the largest among the three surface plots, then it is followed by the surface plot of ethyl acetate and sodium glycol, and the last one is the surface plot of ethylene glycol and sodium benzoate. In the other hand, the surface plot of ethylene glycol and sodium benzoate has the greatest area of the highest value of corrosion rate. Therefore, it can be conclude that the combination of ethyl acetate and ethylene glycol is the most efficient, then followed by the combination of ethyl acetate and sodium benzoate, then the last one is ethylene glycol and sodium benzoate.

In this project, the occurrence of the results may cause by the synergistic effect when the three inhibitors are mixed together. After reviewing a number of journals, there might be some possible situations to occur during the experiment. Sodium benzoate may affect the solubility of ethyl acetate and ethylene glycol in NaCl. When different concentration of sodium benzoate were used, the solubility of other corrosion inhibitors will be different. In addition, the results also can be affected by the combination of ethyl acetate and ethylene glycol since their combination will increase the toxicity. Besides, when ethylene glycol mixed with ethyl acetate, acetic acid in ethylene glycol would be extracted out. Hence, the most synergistic effect of the mixed inhibitor is ethyl acetate and ethylene glycol among the three pairs of inhibitors.

4. Conclusions

From the experiments that have been carried out, it indicates the lowest corrosion rate happened with 300 ppm ethyl acetate, 30 % in water of ethylene glycol, and 300 ppm sodium benzoate whose value is 0.0439 mmPY. The combination of ethyl acetate and sodium benzoate has a medium area of the lowest corrosion rate, where the combination of ethylene glycol and sodium benzoate implies the smallest area of the lowest corrosion rate. From this results, it indicates that the best combination or synergistic effect of the chemicals are ethyl acetate and ethylene glycol. Furthermore, It can be concluded that the selected model adequately represent the data for all responses obtained. Second order polynomial regression model is adequate to represent the data for all responses obtained. Using RSM, further analyses regarding individual and interaction effects between the variables can be study

more comprehensive. Corrosion product formation is an important parameter in defining corrosion model and predicting corrosion rates in systems containing NaCl.

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