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STATISTICAL ANALYSIS OF EFFECTIVE VARIABLE PARAMETERSON CORROSION RATE OF X 52 CARBONS STEEL

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ABSTRACT

Nowadays, carbon and low alloy steels are widely exercised in pipeline construction. By having high pressure of CO_2 which is used for the flooding reservoir, the oil fields lifetime could be increase. Basically, CO_2 are able to dissolve in the existence of the brine water and forming carbonic acid. Carbonic acid could be expressed as a corrosive media. Inhibitor injection method can be used to prevent CO_2 corrosion in the pipeline. Imidazoline is one of the most common corrosion inhibitor which is used to prevent CO_2 corrosion. This inhibitor has high effectiveness towards corrosion mitigation. The corrosion rate is related to various factors such as; temperature, inhibitor concentration, and pH of environment. Inthis study, corrosion rate measurements were done based on weight loss test and linear polarization resistance (LPR) test, the results proved that the corrosion rate will become lower at greater inhibitor concentration. Furthermore, the corrosion rate will greatly increase due to decreasing in pH of the surrounding. Moreover, the corrosion rate will slightly increase as the temperature of the surrounding increase. As an overall conclusion, this research would benefit one to estimate the corrosion rate in different surrounding condition by inserting the values of factor A, B, and C in this provided governing equation harvested by Box Behnken design.

Keywords: carbonic acid, carbon dioxide corrosion, weight loss test, linear polarization resistance test, response surface methodology, box behnken design.

INTRODUCTION

One of the most aggressive environments and most often found in the internal pipeline in petroleum industry is a fluid with a high concentration of chloride and containing carbon dioxide (CO_2) that would lead to CO_2 corrosion which is commonly called as sweet corrosion [1].Currently, mitigation of internal corrosion in the pipeline was done by applying corrosion inhibitors.Inhibitors are substances that are added in small amounts to prevent corrosion. The advantage of using inhibitor as a method of preventing corrosion is, this method does not disrupt the process. The addition of inhibitors (any reagent which can convert an active corrosion process to passive process) can suppress the corrosion rate significantly [2].

Absorption of inhibitors on the metal surface can suppress the electrochemical reaction during corrosion process. Several studies which are conducted on the effectiveness of imidazoline showed that imidazoline could inhibit metal surface with good effectiveness in CO_2 saturated brine solution as the environment [3].In objective to mitigate CO_2 corrosion favorably, imidazoline and its derivatives inhibitor could be the best alternative.

Imidazoline and its derivatives are one of the most effective organic corrosion inhibitor and widely used to protect the pipeline from CO_2 corrosion. The effectiveness of imidazole as an organic corrosion inhibitor obtained because of the absorption of the inhibitor on the metal surface. The corrosion inhibition efficiency of the imidazoline surfactant in 1 M H_2SO_4 solution is 91 percent. This corrosion inhibition efficiency is measured by using weight loss method[18]. Furthermore, imidazoline inhibitor also used to study rate of CO_2 corrosion of X52 steel in carbon dioxide water environment. The result shown that 100ppm concentration of imidazoline have an inhibitor efficiency of 90 percent [7]. The imidazolium ring structure has characteristics which permit it to adsorb onto metallic surfaces with or without corrosion product. The active area of the metallic surface is coated by heterocyclic compound. This metallic surface coverage will act as a barrier between the boundary and corrosive surroundings. Thus, the resistance toward corrosion will be increase and changing the interface reaction measure [19].

Two methods that could be exercised to estimate corrosion rate are linear polarization resistance (LPR) and weight loss method [4–7]. Response Surface Methodology (RSM) method could be used for statistical analysis of the results obtained [8–16].

Parameters that have correlation with the corrosion rate are temperature, corrosion inhibitor concentration, and pH of the environment. As the inhibitor concentration increasing, the porosity of inhibitor films will decrease. In addition, 100 ppm inhibitor concentration would provide better charge transfer resistance compare to 25 ppm. It showed that the corrosion rate will become lower at greater inhibitor concentration[20].

The concentration of H^+in the solution is higher under lower pH value. Thus, the H^+ reduction will become major cathodic measure. Meanwhile, under pH range pH 4-6, the direct reductions of HCO_3^- and H_2CO_3 become important. The dominant cathodic reaction changes to direct reduction of water under high over potential [21]. Thus, the corrosion rate will greatly increase due to decreasing in pH of the surrounding.

As the molecular weight of imidazole derivatives increasing, the corrosion inhibitor efficiency will increase. However, the corrosion rate will increase due to high temperature which is above 40 °C.The higher molecular weight imidazole derivatives reveal better corrosion inhibition and by the fact that the corrosion rate of the carbon steel increasing at higher temperature which is in the range of 40-50 °C [22]. Another study showed that inhibition efficiency will rise as the temperature increase from 25 to 55 °C [23].

Thus, statistical analysis towards parameters that affecting corrosion rate should be done in purpose to increase the conciseness, clarity and objectivity with which results are presented and interpreted. Predicting the optimum concentration of Imidazoline inhibitor used to inhibit the corrosion of refined metal in saltwater saturated with CO_2 is critical and cost effective in the oil and gas industries. Therefore, the aimof this study is to have a statistical analysis of various variable factors that are temperature, pH, and concentration of inhibitor towards corrosion rate.

EXPERIMENTAL PROCEDURS

Response surface methodology (RSM)

Response Surface Methodology (RSM) was used for statistical analysis of the obtained results. The primary objective of RSM is to decide best settings of the control parameters that results in a maximum or minimum response over a certain zone of interest. Previously, RSM was exercised to study the influence of pH, temperature and inhibitor concentration towards corrosion inhibitor efficiency, and the interference between these parameters for aluminum[13]. Box Behnken design is used as an experimental design for Response Surface Methodology. The total number of experiment required for this analysis is seventeen. There are five repetitions of the same manipulated factors present in this experimental design in purpose to validate the accuracy of the experiments results.

Corrosion rate measurement

Weight loss

Flat specimens are usually preferred because of easier handling and surface preparation. First of all, clean the sample to remove any cutting oils. This may be done using soapy water or an appropriate solvent. If necessary, mount the sample in epoxy or a phenolic resin. Grind the specimens using increasingly fine grinding paper. Typically progressing from 180 grit to 240 to 320 to 400 and then finally 600 grit is adequate. Surface should be cleaned thoroughly with an appropriate cleanser after which it should be rinsed in distilled water to remove any traces of the cleanser. The clean, dry specimens should be measured and weighed. Dimension determined to the third significant figure and mass determined to the fifth significant figure are suggested. Prepare 3wt% test solution by mixing 30.9g sodium chloride with 1000ml distilled water. Stir the mixture until it dissolved properly. Purge the solution with CO_2 for about 1 hour or until reach desired pH value (refer Table-1). Temperature of the corroding solution should be controlled within ±1 degree (refer Table-1). The weighed specimen is introduced into the prepared solution. Then, inject the imidazoline inhibitor into the solution and removed after reasonable time interval.

Linear polarization resistance (LPR)

LPR test was done in 1 Liters of 3wt% NaCl by three electrode glass cell and potentiostat equipment. The desired temperature of the solution was controlled by using hot plate. Oxygen level in solution was reduced prior to immerse of specimen. This can be accomplished by purging with CO_2. Prepare the working electrode. Carbon steel samples weregrindedwith 240 grit and 600 grit SiC paper then rinsed with deionized water and degreased with acetone. After that, they were dried. pH of the solution was adjusted by using NaOH and HCl.Desired concentration of corrosion inhibitor was injected to solution.

RESULT AND DISCUSSIONS

Corrosion rate based on weight loss

Corrosion rate can be determined based on the weight recorded. The corrosion rate can be calculated using the following equation (Equation. 8).

$$Corrosion\ rate\ mm/y = \frac{87.6\ x\ mass\ loss}{(area)(time)(metal\ density)} \quad (8)$$

Where test specimen mass loss is expressed in *mg*, area in cm^2 of test specimen, exposure time in *hours*, and the metal density in g/cm^3.

Table-1 shows the design of experiment (DOE) of this study. Based on Figure-1 for Weight Loss Method, the high corrosion rate observed under DOE 9 and DOE 11 which involving high temperature condition, insufficient inhibitor concentration and lower pH of the environment. The large difference in the corrosion rate is observed between DOE 9 and DOE 11, against DOE 1 and DOE 12. This is because the inhibitor concentration and pH give major impact towards corrosion rate. As a conclusion, as the inhibitor concentration increase, the corrosion rate will decrease. Furthermore, the corrosion rate will greatly increase due to decreasing in pH of the surrounding. Lastly, the corrosion rate will slightly increase as the temperature of the surrounding increase.

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Table-1. Design of experiment.

Run	Block	Factor 1 [A: Temperature (Celcius)]	Factor 2 [B: Inhibitor concetration (ppm)]	Factor 3 C: pH
1	Block 1	25.00	50.00	5.00
2	Block 1	50.00	27.50	5.00
3	Block 1	50.00	27.50	5.00
4	Block 1	50.00	5.00	7.00
5	Block 1	25.00	27.50	3.00
6	Block 1	50.00	50.00	3.00
7	Block 1	75.00	50.00	5.00
8	Block 1	50.00	27.50	5.00
9	Block 1	75.00	27.50	3.00
10	Block 1	25.00	5.00	5.00
11	Block 1	50.00	5.00	3.00
12	Block 1	75.00	5.00	5.00
13	Block 1	50.00	27.50	5.00
14	Block 1	50.00	27.50	5.00
15	Block 1	25.00	27.50	7.00
16	Block 1	75.00	27.50	7.00
17	Block 1	50.00	50.00	7.00

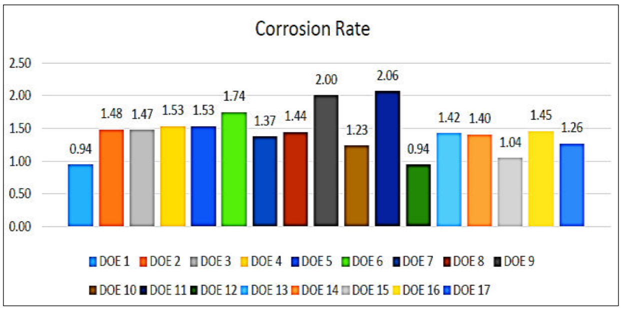

Figure-1. Corrosion rate vs time.

Corrosion rate based on LPR

Based on Table-2, the Box Behnken design is used as an experimental design for Response Surface Methodology. The total number of experiment required for this analysis is seventeen. There are five repetitions of the same manipulated factors present in this experimental design in purpose to validate the accuracy of the experiments results. For the analysis, the transformation used is 'None'. Table-3 shows the experimental design summary.

Table-2. Result of corrosion rate based on LPR method.

Std	Run	Block	Factor 1 [A: Temperature (Celcius)]	Factor 2 [B: Inhibitor concetration (ppm)]	Factor 3 C: pH	Response 1 Corrosion Rate (mm/year)
3	1	Block 1	25.00	50.00	5.00	1.03
13	2	Block 1	50.00	27.50	5.00	1.56
15	3	Block 1	50.00	27.50	5.00	1.59
11	4	Block 1	50.00	5.00	7.00	1.66
5	5	Block 1	25.00	27.50	3.00	1.61
10	6	Block 1	50.00	50.00	3.00	1.85
4	7	Block 1	75.00	50.00	5.00	1.51
17	8	Block 1	50.00	27.50	5.00	1.52
6	9	Block 1	75.00	27.50	3.00	2.09
1	10	Block 1	25.00	5.00	5.00	1.32
9	11	Block 1	50.00	5.00	3.00	2.14
2	12	Block 1	75.00	5.00	5.00	1.78
14	13	Block 1	50.00	27.50	5.00	1.53
16	14	Block 1	50.00	27.50	5.00	1.55
7	15	Block 1	25.00	27.50	7.00	1.13
8	16	Block 1	75.00	27.50	7.00	1.61
12	17	Block 1	50.00	50.00	7.00	1.38

From Table-4, the model is proved as a significant model due to F-value of 333.05. Thus, this implies there is 0.01% of chance that 'Model F-Value' this high could happen due to noise. According to Table-3, terms A, B, C, A^2 and $C^2$are significant and can inhance model validity. Furthermore, the "Lack of Fit F-value" is entitled as 'not significant' which mean the design model is valid.Figure-2 shown the evaluation on predicted results. As an overall observation, most of the actual results point are fall closer towards straight line which indicating that there is no abnormalities.Figure-3 shows that the predicted value for the size of the studentized residual is independent. Thus, the distribution of the studentized residuals will be approximately the same for each manipulated factors. For this case, the plot is accepted.

Table-3. Design summary.

Design Summary							
Study Type	Response Surface	Experiments	17				
Initial Design	Box Behnken	Block	No Blocks				
Design Model	Quadratic						
Response	Name	Units	Obs	Minimum	Maximum	Trans	Model
Y1	Corrosion Rate	mm/year	17	1.03	2.14	None	Quadratic
Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded
A	Temperature	Degree C	Numeric	25.00	75.00	-1.000	1.000
B	Inhibitor Concentration	ppm	Numeric	5.00	50.00	-1.000	1.000
C	pH	pH	Numeric	3.00	7.00	-1.000	1.000

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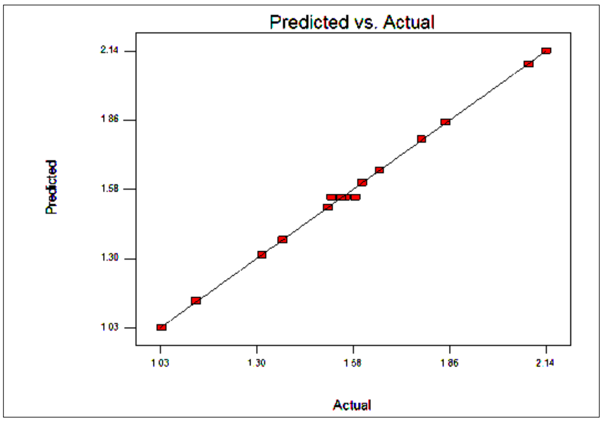

Figure-2. Predicted vs actual.

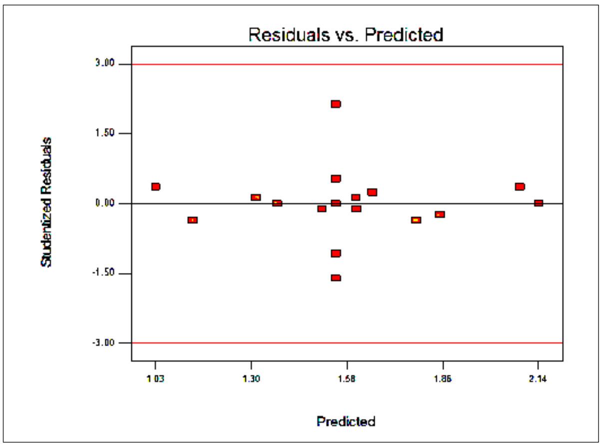

Figure-3. Studentized residual vs predicted.

Table-4. ANOVA for response surface quadratic model.

ANOVA for Response Surface Quadratic Model						
Analysis of variance table [Partial sum of squares]						
Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	1.32	9	0.15	333.05	<0.0001	significant
A	0.45	1	0.45	1027.24	<0.0001	
B	0.16	1	0.16	363.35	<0.0001	
C	0.46	1	0.46	1038.08	<0.0001	
A^2	0.087	1	0.087	198.06	<0.0001	
B^2	5.921E-005	1	5.921E-005	0.13	0.7244	
C^2	0.17	1	0.17	397.91	<0.0001	
AB	1.00E-004	1	1.000E-004	0.23	0.6478	
AC	0.000	1	0.000	0.000	1.0000	
BC	2.500E-005	1	2.500E-005	0.057	0.8183	
Residual	3.075E-003	7	4.393E-004			
Lack of Fit	7.500E-005	3	2.500E-005	0.033	0.9906	not significant
Pure Error	3.000E-003	4	7.500E-004			
Cor Total	1.32	16				

For interpretation of ANOVA table, two items are more important which show the propose model validity. Based on Figure-4, the distribution of the point on the right section of the graph is likely similar to the distribution of the point on the left side. This indicate that the effect of inhibitor concentration is significant at both high and low level of temperature. The gap between both high and low level condition is not greater than interaction of factors AC and BC.

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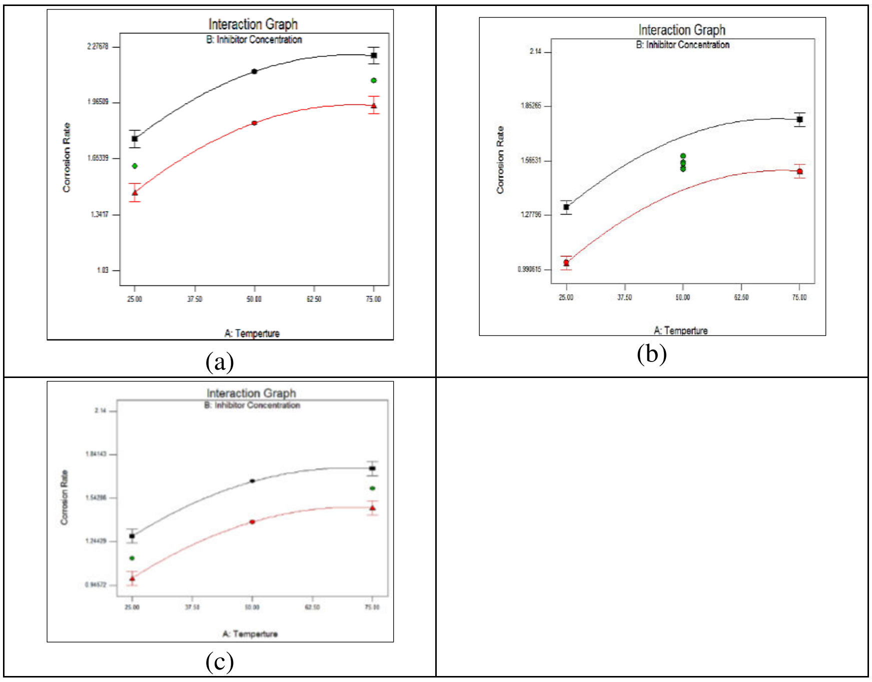

Figure-4. Interaction graph of factors AB with 5ppm (black) and 50ppm (red) corrosion inhibitor concentration under (a) pH 3,(b) pH 5, and (c) pH 7.

Figure-5 show that the distribution of the point on the right section of the graph is likely similar to the distribution of the point on the left side. This indicate that the effect of pH is significant at both high and low level of temperature. The gap between both high and low level condition is greater than interaction of factors AB. Thus, by controlling these followings factor could manage to overcome high response of the corrosion rate.

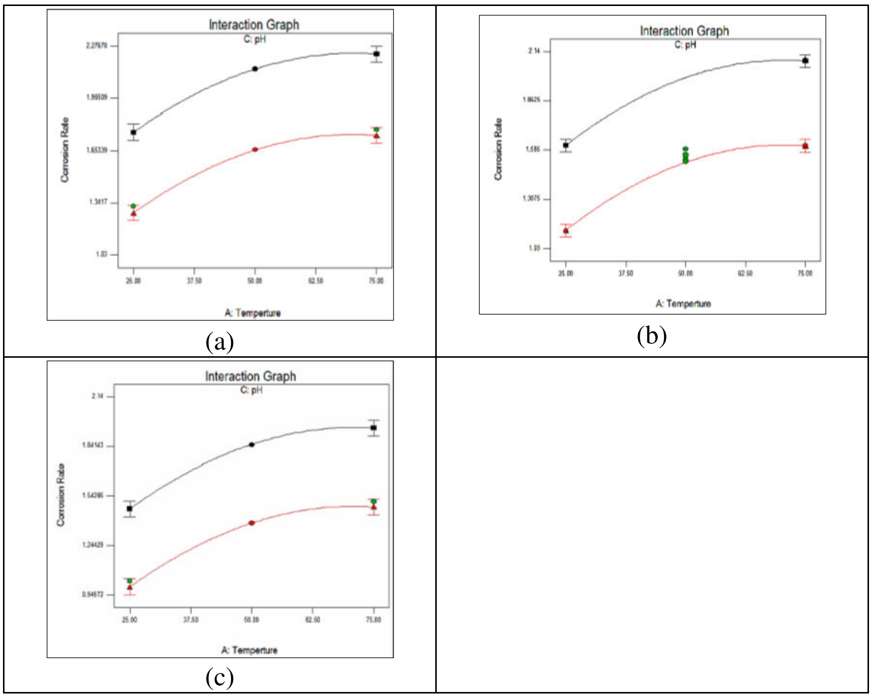

Figure-5. Interaction graph of factors AC with pH 3 (black) and pH 7 (red)under (a) 5ppm,(b) 27.5ppm, and (c) 50ppm corrosion inhibitor concentration.

From Figure-6, it can be approved that the distribution of the point on the right section of the graph is likely similar to the distribution of the point on the left side. This indicate that the effect of pH is significant at both high and low level of inhibitor concentration. The gap between both high and low level condition is greater

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than interaction of factors AB. Thus, by controlling these followings factor could manage to overcome high response of the corrosion rate.As an overall conclusion, the interaction of factors AC and BC provide major impact toward the response of corrosion rate which implies that both of these interaction factors should be critically controlled to get smallest response of corrosion rate.

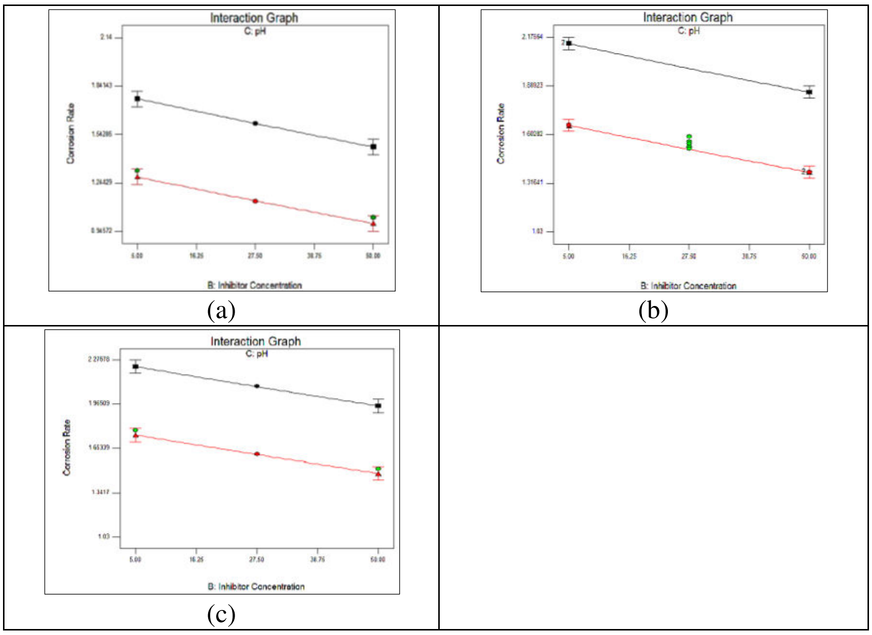

Figure-6. Interaction graph of factors BC with pH 3 (black) and pH 7 (red)under (a) 25, (b) 50, and (c) 75 Degree celcius.

Figure-7 shown cube graph of factor A, B, and C.Factor A,B and C are integrated to provide overall response toward the model response. Estimated values could be obtained based on the belowcube graph without having an actual data. The corrosion rate is maximum at the A+, C-, B- settings which giving value of 2.23mm/year of corrosion rate.

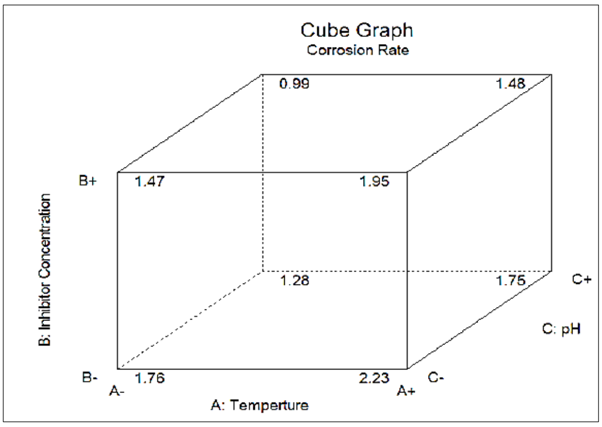

Figure-7. Cube graph.

From Figure-8, it canbe concluded that the distribution of corrosion rate is the lowest under pH 7, 25 degree celcius and 50ppm of inhibitor concentration. For the real practice of controlling the corrosion rate, the user could referring to these 3D factors interaction model to find the optimum inhibitor concentration under specific environment condition.

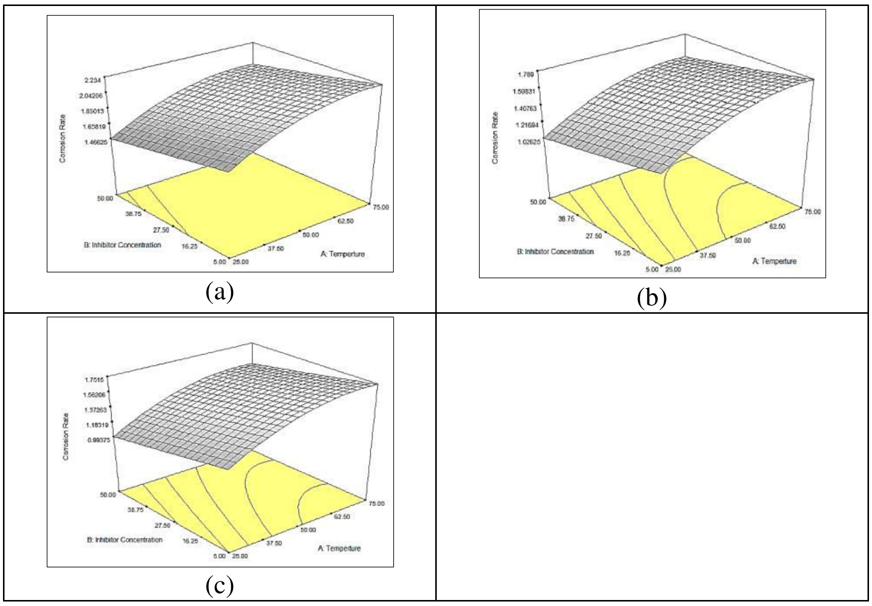

Figure-8. Surface plot of interaction factor AB under (a) pH 3, (b) pH 5, and (c) pH 7.

Another alternative to estimate the corrosion rate in different surrounding is by inserting the values of factor A, B and C in the following equation (Equation. 9) of prediction model in terms of actual factor as stated below. From the equation we can predict that by increasing factors B and C the corrosion rate will decrease. Otherwise, by increasing factor A, the corrosion rate will increase. Furthermore, the equation indicating the significant factor that effect to corrosion rate inthe order of corrosion inhibitor concentration > pH > temperature.

$$\text{Corrosion rate} = +2.56841 + 0.032256 * A - 7.40741E\text{-}003 * B - 0.63028 * C - 2.30000E\text{-}004 A^2 + 7.40741E\text{-}006 * B^2 + 0.050938 * C^2 + 8.8888E\text{-}006 * A * B + 2.13371E\text{-}018 * A * C + 5.55556E\text{-}005 * B * C \quad (9)$$

CONCLUSIONS

In conclusion, creating a new correlation to predict optimum amount of concentration of Imidazoline inhibitor required to inhibit the corrosion of refined metal in saltwater saturated with CO_2 is very critical and important in purpose to reduce financial lost. In addition, statistical analysis of various variable factors that are temperature, pH, and concentration of inhibitor towards corrosion rate are really required in purpose tackle the performance of the inhibitor. Based on weight loss test and linear polarization test, the results proved that as the inhibitor concentration increase, the corrosion rate will decrease. Furthermore, the corrosion rate will greatly increase due to decreasing in pH of the surrounding. Moreover, the corrosion rate will slightly increase as the temperature of the surrounding increase. As an overall conclusion, this research would benefit one to estimate the corrosion rate in different surrounding is by inserting the values of factor A,B and C in this provided governing equation harvested by Box Behnken design.

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