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Modelling and Optimization of Carbon Steel Corrosion in CO_2 Containing Oilfield Produced Water in Presence of HAc

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Abstract

Previously, many empirical models have been used to predict corrosion rates under different CO_2 corrosion parameters conditions. Most of these models did not predict the corrosion rate exactly, besides it determined effects of variables by holding some variables constant and changing the values of other variables to obtain the regression model. As a result the experiments will be large and cost too much. In this paper response surface methodology (RSM) was proposed to optimize the experiments and reduce the experimental running. The experiments studied effects of temperature (40 – 60 °C), pH (3-5), acetic acid (HAc) concentration (1000-3000 ppm) and rotation speed (1000-1500 rpm) on CO_2 corrosion performance of the regression model calculated by RSM. The experiments were conducted in saturated solution of CO_2 with 3.5 % NaCl solution. *STATISTICA* program version 10 was used for data analysis. In conclusion a quadratic model is proposed to predict the effect of mentioned variables in CO_2 environment.

Key Words: CO_2 corrosion, regression analysis, optimization, carbon steel, corrosion rate, full factorial experimental design.

Introduction

The major concern with CO_2 corrosion in oil and gas industry is that CO_2 can cause failure on the equipment due to the hydration to carbonic acid leading to a decrease in pH and initiating the CO_2 corrosion process. Degree of corrosiveness due to CO_2 gas is influenced by environmental conditions such as; temperature, CO_2 partial pressure, corrosion film properties and flow conditions [1, 2].

Many studied on CO_2 corrosion prediction and the effects of species like HAc with several other operating conditions including above mentioned once had been published [3-5]. The simultaneous effects of many variables in the CO_2 corrosion could be optimized by using a statistical methodology such as design of experiment.

In CO_2 corrosion, iron carbonate ($FeCO_3$) film is the chief corrosion product formed and is formed through the reaction between carbonic acid, source of carbonate ions, (CO_3^{-2}) and iron (Fe^{+2}) released through corrosion of the pipeline. $FeCO_3$ forms on the wall of the pipe if the product of ferrous ion concentration (Fe^{+2}) and carbonate ion concentration (CO_3^{-2}) exceeds the solubility product limit. The film is known to be protective and the corrosion rate drops once the film starts growing. Although iron carbonate film formation mechanisms and kinetics have been extensively studied, it is not known how protective the film will be in the presence HAc. Moreover it is not known if the film failure (if any) is a result of a lower system pH or the result of interaction between corrosion products and HAc. Thus it becomes imperative to understand how $FeCO_3$ precipitation is affected in the presence of HAc, as also by the pH, temperature and ionic strength of the solution [6].

Experimental Work

Electrochemical Set-up & Specimen Preparations

A typical schematic three–electrode set-up used in all electrochemical experiments is shown in Fig. (1). A rotating cylinder electrode with a speed control unit was used as the working electrode.

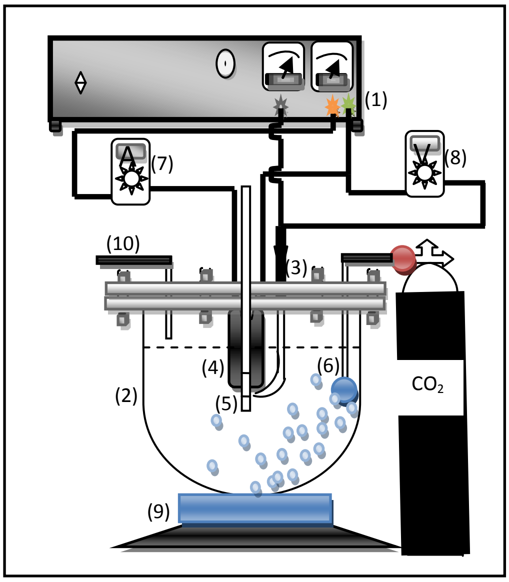

Fig.1, Schematic Corrosion Test Cell [7].

1. Potentiostat	6. CO_2 Gas Distributer
2. Corrosion Test Cell	7. Ammeter
3. Reference Electrode	8.Voltmeter
4. Counter Electrode	9. Hot Plate
5. Working Electrode	10. CO_2 Gas Outlet

Glass cell was fitted with graphite electrode as auxiliary electrode and SCE as a reference electrode. The working electrodes were API X65 carbon steel and the chemical composition is shown in table (1). The cylindrical specimens have diameter of 2.03 cm and 2.08 cm length with 0.13 cm thickness. Before immersion, the specimen surfaces were polished successively with 220, 320, 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.

Table 1, Composition of API X65 Carbon Steel in the Experiments

API X65	wt%
C	0.15
Si	0.24
Mn	1.34
P	0.01
S	0.004
Mo	0.10
Fe	Balance

Cell Solutions

The experiments were performed both in stagnant and flow solution. The total pressure was 1 bar, the glass cell was filled with 1 liter of distilled water and 3.5% wt. NaCl which was stirred with magnetic stirrer. The CO_2 gas (> 99.99 %) was bubbled through the cell (at least 1 hr prior to experiment) in order to saturate and de aerate the solutions. Temperature was set using a hot plate. After the solution was prepared, the pH was adjusted to reach the pH set by using $NaHCO_3$ and HCl, as buffer solutions. Simulation of flow condition was conducted using rotating cylinder electrode (RCE). A cylindrical working electrode was screwed on to an electrode holder at the center of the cell for rotating in the RCE. The weight loss technique was used to measure the corrosion rate in gm/m^2.day (gmd).

Variable Coding and Experimental Design

Two levels Full Factorial Experimental Design (FFED), with four variables, was used to study the response pattern and to determine the combined effect of variables. The effect of independent variables of T (°C), pH, HAc concentration C_A (ppm) and ω (rpm) is shown in table (3). The experiments number 17-20 were used to allow for estimating for a pure error of mean squares. The variables were coded according to the following Equation [8].

$$x_{\text{code}} = \frac{2(X - X^{\text{cent.}})}{(X^{\text{max.}} - X^{\text{min.}})} \qquad \dots (1)$$

Where x_i= coded value of an independent variable.

X_i= real value of an independent variable.

Table 2, shows the real and coded variables used in RSM study.

	Real	T (°C)	pH	HAc (ppm)	ω (rpm)
	Code	x_1	x_2	x_3	x_4
Max. Point	+1	60	5	3000	1500
Center Point	0	50	4	2000	1250
Min. Point	-1	40	3	1000	1000

Table (3) shows a full factorial 2-levels experimental design, with four variables (coded & real) was used to study response pattern & to determine the combination effects of variables.

Table 3, two-level full factorial experimental design of the independent Variables with the observed, predicted values and absolute percentage error for the response.

Run No.	Coded factor				Response (gmd)			Error $\lvert\delta_i\rvert$[%]
	x_1	x_2	x_3	x_4	C.R	$C.R_P$	Exp. Error $= C.R - C.R_P$	
1	-1	-1	-1	-1	48.52	48.72	-0.20	0.41
2	+1	-1	-1	-1	121.30	121.78	-0.48	0.39
3	-1	+1	-1	-1	40.06	39.87	0.19	0.47
4	+1	+1	-1	-1	50.19	49.71	0.48	0.96
5	-1	-1	+1	-1	51.22	51.21	0.01	0.02
6	+1	-1	+1	-1	129.39	128.72	0.67	0.52
7	-1	+1	+1	-1	42.53	42.53	0.00	0.00
8	+1	+1	+1	-1	56.14	56.82	-0.68	1.21
9	-1	-1	-1	+1	52.65	52.76	-0.11	0.21
10	+1	-1	-1	+1	125.15	124.37	0.78	0.62
11	-1	+1	-1	+1	43.67	43.55	0.12	0.27
12	+1	+1	-1	+1	51.14	51.93	-0.79	1.54
13	-1	-1	+1	+1	55.69	55.38	0.31	0.56
14	+1	-1	+1	+1	130.46	131.43	-0.97	0.74
15	-1	+1	+1	+1	46.02	46.33	-0.31	0.67
16	+1	+1	+1	+1	60.14	59.16	0.98	1.63
17	0	0	0	0	63.81	61.15	2.66	4.17
18	0	0	0	0	59.72	61.15	-1.43	2.39
19	0	0	0	0	62.43	61.15	1.28	2.05
20	0	0	0	0	58.64	61.15	-2.51	4.28
The mean absolute percentage error $\lvert\bar{\delta_i}\rvert$ = 1.2 [%]								

Results and Discussion

Fitting the Model

Data from full factorial experimental design as given in table (3) was analysed by the least squares method to fit the second order polynomial model given the Eq. (2), which represents an empirical relationship (in coded values and real units).

$$C.R_P = 61.15 + 21.47\,\mathrm{T} - 20.28\,\mathrm{pH} + 2.43C_A + 1.6\,\omega + 1.97\,\mathrm{T}^2 + 1.97\mathrm{pH}^2 + 1.97{C_A}^2 + 1.97\omega^2 - 15.8\,\mathrm{T\,x\,pH} \quad \ldots(2)$$

Where, T = Temperature (°C)
pH = Acidity or Strength of CO_2 Saturated Solution
C_A = Concentration of HAc (ppm)
ω = Rotation Speed (rpm)

Statistical Analyses

It appears that the presented model significantly represents the data as described in table (4). Table (4) shows the analysis of variance for corrosion in saturated CO_2 solution using Full Factorial Experimental Design (FFED) Methodology. The main factors for the coefficient of the linear and square models shows significant value at confidence level of $\alpha = 0.05$ ($p < 0.5$). However, for the interaction effect of the model is insignificant ($p > 0.5$) except for (T x pH). Furthermore, the high value (99.99 %) of the correlation coefficient (R^2) for the responses suggests that the model is a good fit.

Table 4, Analysis of Variance (ANOVA) for the Fitted Model

Const. Estim^d	Source	$\sum x^2$	Estim. Coeff. (b)	Variance $S_b{}^2 = S_r{}^2/\sum x^2$	F-value $= b^2/S_b{}^2$	$F_{0.95(1,5)} = 6.61$
b_1	Linear	16	21.5	0.3	1685.9	S
b_2		16	-20.3	0.3	1503.9	S
b_3		16	2.4	0.3	21.6	S
b_4		16	1.6	0.3	9.3	S
b_{11}	Square	16	1.9	0.3	14.1	S
b_{22}		16	1.9	0.3	14.1	S
b_{33}		16	1.9	0.3	14.1	S
b_{44}		16	1.9	0.3	14.1	S
b_{12}	Interaction	16	-15.8	0.3	913.3	S
b_{13}		16	1.1	0.3	4.5	NS
b_{14}		16	-0.4	0.3	0.5	NS
b_{23}		16	0.04	0.3	0.01	NS
b_{24}		16	-0.1	0.3	0.03	NS
b_{34}		16	0.03	0.3	0.004	NS

Model Adequacy Checking

The accuracy of any empirical model can also be done by means of statistical parameters, for example, correlation coefficient. The correlation coefficient (R^2) is a statistical measure of the strength of correlation between the predicted and measured values [9]. For the current problem, the following result is obtained: $R^2 = 0.999$ in presence of acetic acid (absence of the protective film formation) as shown in Fig. (2).

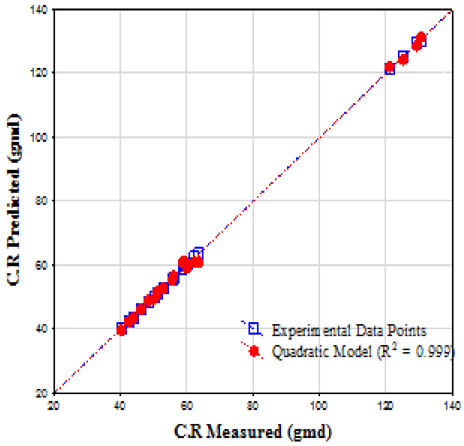

Fig. 2, Performance of the Quadratic Mathematical Model for API X65 Mild Steel in Presence of Acetic Acid (Absence of Protective Film Formation)

Graphic Analysis of the Model

The aim of this study was to find a corrosion rate whose features would have been previously defined from the operative conditions extracted from the quadratic mathematical model.

Because the direct exploitation of the Equation was delicate, it was convenient to restore it under a graphic representation; while fixing two of the four factors of the survey, it was possible to represent the response surface materializing the surface of regression in a three-dimensional space. It was also possible to project the equation in a design under isoresponse curves, interpreted as card curves level.

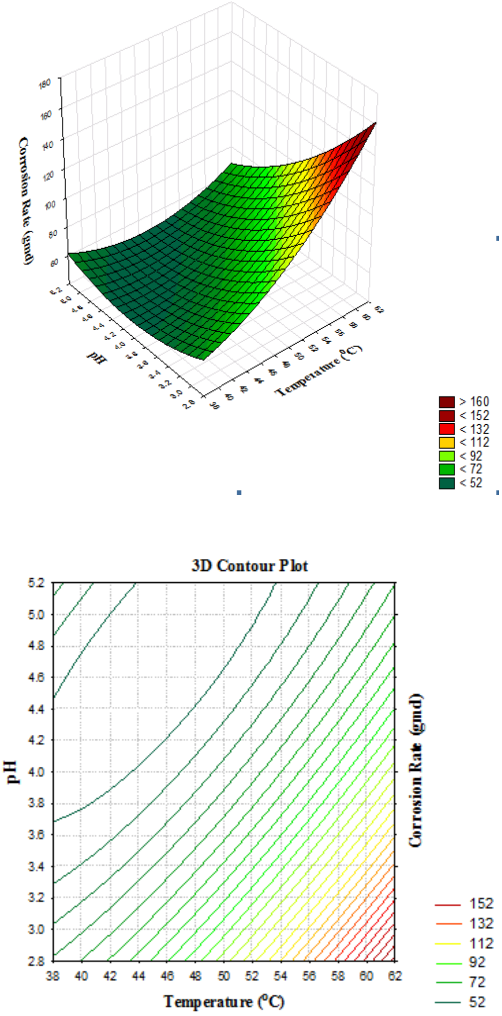

Fig. 3, Response Surface Plot (top) and Contour Plot (bottom) Showing the Variation of Response (Corrosion Rate) as a Function of the Temperature and pH at the Optimum Conditions (2178.5 ppm HAc & 1296.6 rpm).

(i) Evolution of Corrosion Rate as a Function of the Temperature and the pH

Fig. (3) shows the evolution of the corrosion rate as a function of the temperature and the pH. It can be seen that the temperature has a strong influence on the tentative response. The minimal corrosion rate is obtained for a temperature of -0.5 in coded variable, i.e., 45.4 °C in real variable. Considering simultaneous effects of temperature and pH is presented in Fig. (3) contour plot. The Figure shows, in low pH (pH 3), the increase of corrosion rate is higher than in higher pH (pH 5).

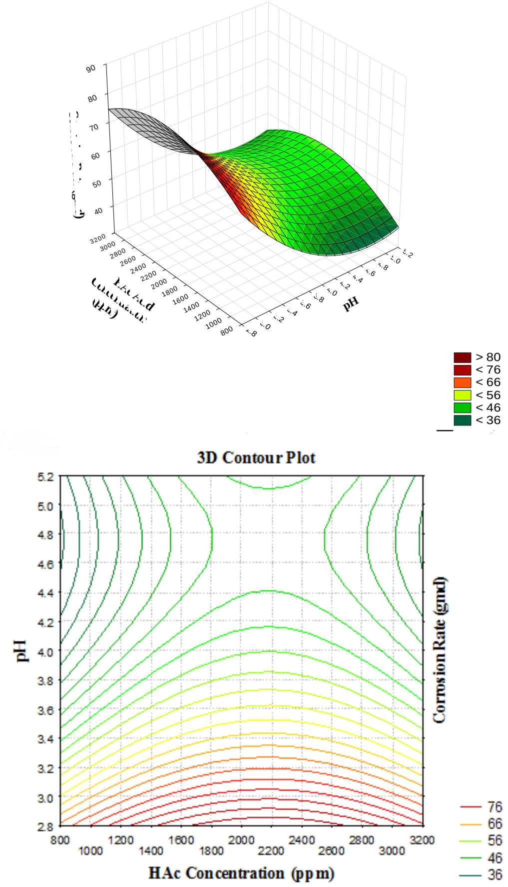

Fig. 4 Response Surface Plot (top) and Contour Plot (bottom) showing the Variation of Response (Corrosion Rate) as a Function of the pH and HAc Acid Concentration at the Optimum Conditions (45.4 °C & 1296.6 rpm

(ii) Evolution of Corrosion Rate as a Function of the pH and HAc Acid Concentration

Fig. (4), shows the synergism between the two factors: the pH and HAc acid concentration in corrosion rate at temperature 45.4°C and speed of rotation of 1296.6 rpm. It can be noted that the effect of the HAc acid concentration differed according to the corrosion rate's variation. This effect becomes positive and even more important when the corrosion rate is degraded (reduced). Analysis of corrosion rate as effects of interaction between pH and HAc acetic concentration is shown in Fig. (4) contour plot. The model shows an increase of corrosion rate due to HAc. And the decrease of corrosion rate is caused by pH.

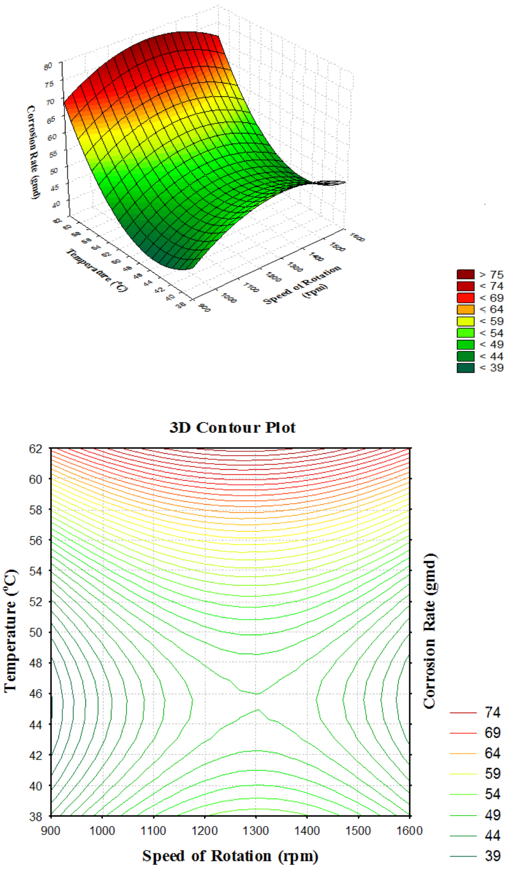

Fig. 5, Response Surface Plot (top) and Contour Plot (bottom) Showing the variation of Response (Corrosion Rate) as a Function of the Temperature and Speed of Rotation at the Optimum Conditions (pH 4.8 & 2178.5 ppm).

(iii) Evolution of Corrosion Rate as a Function of the Temperature and Speed of Rotation

Fig. (5) represent the evolution of the corrosion rate as a function of the temperature and the speed of rotation. This Figure shows that the corrosion rate decreased when the temperature decreased. This evolution was however more accentuated for the lower speeds of rotation. Considering simultaneous effects of temperature and speed of rotation is presented in Fig. (5) contour plot. The Figure shows, in high speed of rotation (1500 rpm), the increase of corrosion rate is higher than in lower speed of rotation (1000 rpm).

(iv) Evolution of Corrosion Rate as a Function of the HAc Acid Concentration and Speed of Rotation

Fig. (6), represent the evolution of the corrosion rate as a function of the HAc acid concentration and the speed of rotation. This Figure shows that the corrosion rate decreased when the HAc acid concentration and speed of rotation decreased.

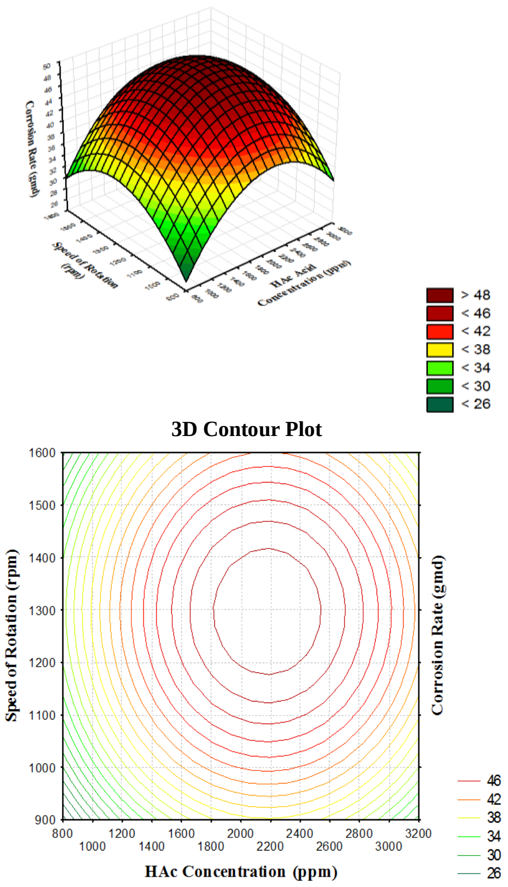

Fig. 6 Response Surface Plot (top) and Contour Plot (bottom) showing the Variation of Response (Corrosion Rate) as a Function of the HAc Acid Concentration and Speed of Rotation at the Optimum Conditions
(45.4 °C & pH 4.8)

This evolution was however more accentuated for the weakest and strongest concentrations in HAc acid and the lessest and greatest effects of speed of rotation. Fig. (6) contour plot presents a polynomial surface response relating to effect of HAc and speed of rotation on corrosion rate. It is shown that different corrosion rate is observed for HAc concentration and speed of rotation. Speed of rotation increased corrosion rate from 26-38 gmd along the speed setting (1000-1500 rpm). HAc concentration from 1000-3000 ppm has increased corrosion rate from 26-42 gmd. [10] and [11] have studied effects of speed of rotation on corrosion rate. They believed effects of mass transfer, hydrodynamic and diffusion coefficient that influenced corrosion rate.

Conclusions

1- The second order polynomial regression analysis of the objective function (corrosion rate) describe the behavior of the process in absence of the protective film formation with mean absolute percentage error 1.2 % in terms of temperature, solution pH, HAc acid concentration and speed of rotation.

2- The corrosion rate of API X65 mild steel in CO_2 saturated, 3.5 wt% NaCl solution in presence of acetic acid, increases with increasing temperature, acetic acid concentration and speed of rotation, and decreased with increasing of solution pH.

3- The optimum conditions as predicted from Eq. (2) are 45.4 °C, pH 4.8, 2178.5 ppm HAc and 1296.6 rpm in absence of the protective film formation.

4- The analysis of statistical Full Factorial Experimental Design (FFED), generally, shows that the square and interaction effects on the corrosion rate by weight loss technique (within the studied range) is less pronounced compared with the main variables except the high interaction effect of (T x pH) in presence of acetic acid.

5- The effect of the temperature, solution pH, HAc acid concentration and speed of rotation on the corrosion rate in absence of the protective film formation in the following order:
Temperature > pH > HAc Acid Conc. > Speed of rotation

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