Predicting Temperature of Corrosion Scale Formation Carbon Steel in Oil and Gas Environment

Y.P. Asmara, Jeya Gopi Raman, A.G.E. Sutjipto

1Mechanical Engineering, Faculty of Engineering and Quantity Surveying
INTI International University, Nilai, Negeri Sembilan, Malaysia
2Faculty of Science and Technology Industry, Universiti Malaysia Pahang
Pekan, Pahang, Malaysia

Email: yuli.pancaasmara@newinti.edu.my

Abstract

Formation of scales on the metal surface during corrosion process in oil and gas environment is one of the important parameter in predicting corrosion rate. The scales are formed on metal surface at specific temperature. Quality of the scales depend on service temperature, concentration of carbon-dioxide (CO₂) and acetic acid (HAc) as main elements in oil and gas environments. This research aims to determine scale formation temperature on of carbon steel under different concentration of CO₂ and HAc using mathematics formulas. The corrosion rate for carbon steel was calculated using linear resistance polarization (LPR) test methods. Specimens were placed in a beaker contained 3.5% NaCl connected to a CO₂ cylinder for CO₂ gas bubbling. The corrosion tests were conducted at room temperature, 60 °C and 80°C in several concentration of CO₂ and HAc. A statistical analysis with response surface methodology (RSM) was used to process the model to predict corrosion scale temperature using second-degree model mathematics formulas. An attempt will also be made to verify the results using data literatures. As results, the predictions show in acceptable ranges (70% – 80 %) as compared to experimental data from literatures.

Keywords

Corrosion scales temperature, Corrosion predictions models, Oil and gas environments, Carbon steel.

Introduction

Oil and gas environment which are exposed to sour/sweet conditions, mostly in transportation pipeline, are covered with corrosion products scales such as FeCO₃ and FeAc when acetic acid (HAc) and Carbon-dioxide (CO₂) present in the oils (Asmara, 2009; Asmara, 2011; Videm, 1994). These types and quality of corrosion products vary depend on temperature, pressure and flow rate (Nesic et al, 2007; Asmara, 2015, et al, 2010; Lee et al., 2004; Wei et al, 2006 . It can determine types of damages to the pipelines which leads to pitting corrosion, cracking and scale detachment (spalling) of the pipeline material. They will affect on corrosion rate (Asmara at al., 2011; Asmara et al., 2016; Nyborg et al., 2006). The other contaminants such as H₂S, NaCl, types of pipelines materials, and inhibitors will also contribute to the
corrosion rate. Studies have demonstrated that those multi species factors can govern the corrosion process in many ways and in several mechanisms.

One of the most important parameter which determines corrosion scale is temperature. Temperature affects the conditions for formation of the protective carbonate layers and affects corrosion rate in a different manner. At temperatures lower than 60 °C, the solubility of FeCO₃ is high and the precipitation rate is slow; thus protective films will not form until the pH is increased more than solubility product (Asmara et al., 2013; Asmara et al., 2012). At that temperature, hydrogen evolution acts as the rate determinating step. At temperatures above 100°C, there is a direct reaction between steel and water to produce dense and protective films. Carbon steel will face problems with pitting and stress corrosion cracking because carbonate film is formed rapidly at 80° C (Nesic et al., 2007).

Methodology

Specimen preparation and test matrix

The working electrodes were made of carbon steel and the chemical composition is as shown in Table1. The cylindrical specimens were of 12 mm diameter and 10 mm long. Before immersion, the specimen surfaces were polished successively with 240, 400 and 600 grit SiC paper, rinsed with methanol and degreased using acetone. The test matrix used to carry out the experiment is presented in Table 2.

Table 1. Composition of 080A15 carbon steel used in the experiments.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C (%)</th>
<th>Si (%)</th>
<th>Mn (%)</th>
<th>P (%)</th>
<th>S (%)</th>
<th>Cr (%)</th>
<th>Ni (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>080A15</td>
<td>0.14</td>
<td>0.175</td>
<td>0.799</td>
<td>0.01</td>
<td>0.03</td>
<td>0.06</td>
<td>0.065</td>
</tr>
</tbody>
</table>

Table 2. Experimental matrix used in the test.

<table>
<thead>
<tr>
<th>Steel Type</th>
<th>080A15 (BS 970)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous solution</td>
<td>3 wt% NaCl,</td>
</tr>
<tr>
<td>Purged gas</td>
<td>CO₂</td>
</tr>
<tr>
<td>Total pressure</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C - 100°C</td>
</tr>
<tr>
<td>Rotation rate</td>
<td>Static</td>
</tr>
<tr>
<td>pH</td>
<td>4 - 6</td>
</tr>
<tr>
<td>Measurement techniques</td>
<td>Linear polarization resistance (LPR)</td>
</tr>
</tbody>
</table>

Static test set-up

The linear polarization resistance (LPR) technique was used to measure the corrosion rate. The procedure was similar as the ASTM experimental test G 5-94 (ASTM standard).

Cell solutions

The experiments were performed in stagnant condition. The total pressure was 1 bar, and the glass cell was filled with 1 litter of distilled water with 3% wt NaCl which was stirred with a magnetic stirrer. Then CO₂ gas was bubbled through the cell in order to saturate and de-aerates
the solution. After the solution was prepared, the pH was adjusted to reach the determined pH by using NaHCO$_3$ as a buffer solution. During the experiment, constant concentration of gases was continuously bubbled through the electrolyte in order to maintain consistent water chemistry.

**Model Regression**

**Second-order model regression**

There is a curvature of general second order model which expressed as:

$$ Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i<j} \sum_{j=1}^k \beta_{ij} X_i X_j + \epsilon $$

where $Y = \text{response that can fit the following linear, quadratic, or cubic regression models:}$

\[ \hat{y}_i = \text{fitted response} \]

\[ Y = \text{response} \]

\[ X_k = \text{k}^{th} \text{ predictor} \]

\[ \beta_k = \text{k}^{th} \text{ population regression coefficient} \]

**Response surface methodology**

Response surface methodology (RSM) with central composite design (CCD) is used to optimize process conditions (Asmara., et al, 2019). It is used to determine the influence of factors as mentioned in the Table 2. Through RSM and applying second order model regression, temperature scale is obtained.

**Results and Discussion**

**Scaling temperature**

Based on the literature reviews (Hunnik., et al, 1996; wei, 2002; Parakala, 2005; Yuhua 2002; Vera, 2006; George, 2004) it is known that effect of temperature increases corrosion rate until the temperature reaches a maximum value called scaling temperature. Beyond this temperature, the corrosion rate will decrease or becomes constant. Factors affecting the scaling temperature are pH and HAc concentration. The scaling temperature as effects of pH predicted by the RSM models are presented in Figure 1.
From Figure 1, it can be seen that higher pH tend to decrease scaling temperature. This observation is supported by several researchers, who related this phenomena to film formation where higher pH tend to favor film precipitation.

Figure 2. Effects of HAc on scaling temperature as calculated by RSM at conditions: stagnant, pH 6, total pressure 1 bar, and 3% NaCl CO$_2$ saturated solution.
Scaling temperature is also influenced by HAc concentration. As shown in Figure 2 and Figure 3, higher HAc concentration will increase scaling temperature. The finding are also supported by (Ismail, 2005). A comparison between calculations from RSM and experimental data is presented in Figure 2. (George, 2004) explained that the presence of HAc can interrupt the film formation and increase scaling temperature. Surface analyses investigation indicated that HAc concentration has decreased the thickness of the film.

Conclusions

Mechanism corrosion rate in CO₂/HAc system
- The introduction of 100 ppm of HAc to the CO₂ gaseous mixture causes the corrosion rate to increase sharply in the temperature range 60–70°C.
- HAc is the dominant factor that governs the reaction process in CO₂ system. The behavior of cathodic reaction consists of chemical reaction and diffusion process.
- Based on mathematics model, the scaling temperature will increase as HAc concentration increases.
- Scaling temperature decreased when pH increased.
- The results have shown that second-order polynomial model can be used to predict CO₂/HAc corrosion pattern adequately.
- This study has proven that central composite experimental design can be applied to predict CO₂ corrosion process with reasonable planning and execution. Thus, the statistical analysis and evaluations of data could be proved analytically.
- Although this models reach reasonable results, the precision can be improved by considering more parameters conditions.

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References