Corrosion Inhibition of Carbon Steel in SULFIRAN® Process

Jaber Neshati*1, Esmaeil Akbarinezhad1, Khaled Forsat2, Masih Hosseini Jenab3, and Bijan Pouryamin4

1 Corrosion Department, Research Institute of Petroleum Industry (RIPI), Tehran, Iran
2 Engineering and Process Development Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran
3 Gas Science Department, Research Institute of Petroleum Industry (RIPI), Tehran, Iran
4 Development and Optimization of Energy Technologies Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

ABSTRACT
In this investigation, attempts were directed to study the inhibitive effects of nitrite and phosphate base inhibitors for the carbon steel alloy samples, which are used in an acid gas treatment process (The SULFIRAN® solution), in Fe-EDTA solution. Electrochemical techniques, i.e. polarization curves and electrochemical impedance spectroscopy (EIS), were used to evaluate the inhibition efficiency. Linear polarization resistance (LPR) and weight loss techniques were also used to determine the corrosion rate for the pilot tests. The results indicated that adding inhibitors reduced corrosion rate to some suitable values (<5 mils per year (mpy)). For both inhibitors, the inhibition efficiency increased with the inhibitor concentration. The results showed that the inhibition efficiency of the phosphate base inhibitor was less than the nitrite base inhibitor.

Keywords: SULFIRAN® Process, Iron Chelate Solution, Corrosion Inhibition, Carbon Steel

INTRODUCTION
There are three main methods of removing H2S from gas streams [1-3]:
1) Liquid and solid H2S scavengers such as triazines and iron sponges;
2) Liquid redox processes, employing aqueous-based solutions containing metal ions, usually iron, which are capable of transferring electrons in any redox reactions;
3) Cluse systems.

SULFIRAN® is a liquid redox process; this is a special technology developed by Research Institute of Petroleum Industry (RIPI) and has the 99.9% H2S removal efficiency. In the SULFIRAN® process, the iron chelate solution, which is used as a catalyst for H2S removal, has been licensed by RIPI. This process is highly flexible and can be used for a wide variety of H2S containing gases. Figure 1 shows the schematic of SULFIRAN® process.

In the plant, the chemistry of SULFIRAN® steps is conducted in two general process environments. These are the H2S catalyst contact area (absorber) and the catalyst regeneration area (oxidizer). In initial steps, the ionized H2S is converted to elemental Sulfur. The ionization steps are as follows:
Next, the ferrous ions will be re-oxidized to ferric ions and the catalyst will be regenerated.

\[
\frac{1}{2} O_2(aq) + H_2O(aq) + Fe^{2+}(aq) \rightarrow 2OH^-(aq) + H^+(aq) + Fe^{3+} \quad (5)
\]

Now, the regenerated catalyst is ready for use in the absorber section again. The overall reaction is shown in Equation 6.

\[
H_2S + \frac{1}{2} O_2 \rightarrow H_2O + S \quad (6)
\]

In this work, the corrosion inhibition of carbon steel alloy in SULFIRAN® solution in the presence of nitrite and phosphate base inhibitors was investigated by using lab and pilot tests.

The inhibition efficiency (IE) of the added inhibitor is obtained by weight loss measurements using the following equation [4]:

\[
IE\% = \frac{W_L - W_{Li}}{W_L} \times 100 \quad (7)
\]

where, \( W_L \) and \( W_{Li} \) are the weight losses with and without adding inhibitors respectively.

**EXPERIMENTAL PROCEDURES**

Coupons and electrodes with ferrite/pearlite microstructures and the chemical composition of Fe=98.7 wt.%, C=0.22 wt.%, Si=0.273 wt.%, Mn=0.553 wt.%, P<0.005 wt.%, S<0.005 wt.%, Cr< 0.0564 wt.%, Mo<0.0142 wt.%, Ni<0.0560 wt.%, Co<0.02 wt.%, Cu<0.0639 wt.%, Nb<0.0144 wt.%, Ti<0.005 wt.%, V<0.005 wt.%, W<0.04 wt.%, Pb<0.01 wt.%, and Zn <0.003 wt.% were cut from a carbon steel tube. The lab and pilot test samples were 5 cm² and 36 cm² in size respectively. The samples were polished with emery paper up to 800 grit and were cleaned in distilled water and degreased in acetone. The base electrolyte was SULFIRAN® solution. All the test solutions were prepared from analytical grade reagents and distilled...
water. The tests were carried out at 43±2 °C. A standard electrochemical cell with three electrodes was used to measure the impedance and potentiodynamic polarization. A carbon steel specimen was used as the working electrode (WE) and a pair of graphite rods as the counter electrode (CE). A saturated calomel reference electrode (SCE) was brought into close proximity with WE by a luggin capillary. The test solution was aerated with dry air or de-aerated with CO₂ (98.4 v/v%)/H₂S (1.6 v/v%) for the corrosion tests. The electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements were performed by the Potentiostat/Galvanostat (model 273A EG&G) and SI (HF Frequency response analyzer). The EIS measurements were carried out at open circuit potential (OCP) with an amplitude of 5 mV AC potential in the frequency ranges of 10⁴ Hz to 0.01 Hz. The EIS curves were simulated by Z-view software. The potentiodynamic polarization tests were performed at a scan rate of 1 mV.s⁻¹ in the applied range of ±300 mV vs. OCP. The electrochemical tests were carried out in a stagnant condition and the flow effect was studied in the pilot tests. The schematic of the pilot plant is shown in Figure 2.

RESULTS AND DISCUSSION

The potentiodynamic polarization curves are shown in Figures 3 and 4 for the carbon steel alloy in SULFIRAN® solutions with different concentrations of nitrite and phosphate base inhibitors.

![Figure 3: Potentiodynamic polarization curves of carbon steel in the SULFIRAN® solution in the presence of nitrite base inhibitor, (1) Blank, (2) 0.05 g/l, (3) 0.075 g/l, and (4) 0.1 g/l](image-url)

Corrosion kinetics parameters such as corrosion potential \(E_{corr}\), corrosion current density \(I_{corr}\), anodic Tafel slope \(b_a\), and cathodic Tafel slope \(b_c\) were deduced from the curves and are given in Table 1. It was found that adding inhibitors decreased corrosion current with respect to the...
It is found that the protective oxide film is formed in the presence of nitrite according to the following reaction [4].

$$4Fe + 3NO_2^- + 6H^+ \rightarrow 2yFe_2O_3 + NH_3 + N_2$$  \hspace{1cm} (8)

In addition, phosphates show corrosion inhibition behavior in the presence of oxygen. The dissolved oxygen in the system oxidized iron to form $\gamma$Fe$_2$O$_3$ and caused the discontinuities in the oxide film to be filled by ferric phosphate [4].

$$Fe^{2+} + H_2PO_4^- \rightarrow FeH_2PO_4^+$$  \hspace{1cm} (9)

$$FeH_2PO_4^+ + 2H_2O \rightarrow FePO_4 + 2H_2O + 2H^+ + e$$  \hspace{1cm} (10)

The Nyquist representation of the electrochemical impedance plots for carbon steel samples in the SULFIRAN® solution containing nitrite and phosphate base inhibitors during the immersion time are presented in Figures 5 and 6 respectively.

Table 1: Electrochemical parameters for the corrosion of carbon steel in a SULFIRAN® solution in the presence of inhibitors

<table>
<thead>
<tr>
<th>Concentration of Inhibitor (w/w%)</th>
<th>$E_{corr}$ (mV vs. SCE)</th>
<th>$b_a$ (mV/dec)</th>
<th>$b_c$ (mV/dec)</th>
<th>C.R (mpy)</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-483.5</td>
<td>113</td>
<td>1281</td>
<td>295</td>
<td>-</td>
</tr>
<tr>
<td>Nitrite base</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>-584.6</td>
<td>125</td>
<td>276</td>
<td>42.6</td>
<td>85.56</td>
</tr>
<tr>
<td>0.075</td>
<td>-229</td>
<td>126</td>
<td>161</td>
<td>3.6</td>
<td>98.78</td>
</tr>
<tr>
<td>0.1</td>
<td>-192</td>
<td>111</td>
<td>62</td>
<td>1.5</td>
<td>99.49</td>
</tr>
<tr>
<td>Phosphate base</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-578</td>
<td>248</td>
<td>237</td>
<td>95.5</td>
<td>67.63</td>
</tr>
<tr>
<td>2</td>
<td>-349</td>
<td>213</td>
<td>267</td>
<td>17.59</td>
<td>94.04</td>
</tr>
<tr>
<td>3</td>
<td>-237</td>
<td>100</td>
<td>100</td>
<td>11.84</td>
<td>95.99</td>
</tr>
<tr>
<td>4</td>
<td>-320</td>
<td>115</td>
<td>221</td>
<td>15.5</td>
<td>94.74</td>
</tr>
<tr>
<td>5</td>
<td>-179</td>
<td>638</td>
<td>94</td>
<td>1.19</td>
<td>99.6</td>
</tr>
</tbody>
</table>

Figure 4: Potentiodynamic polarization curves of carbon steel in the SULFIRAN® solution in the presence of phosphate base inhibitor, (1) 1 wt.%,(2) 2 wt.%, (3) 3 wt.%, (4) 4 wt.%, and (5) 5 wt.%
Corrosion Inhibition of Carbon Steel in SULFIRAN® Process ...  

Figure 5: Nyquist representation of the electrochemical impedance plots for carbon steel alloy in the SULFIRAN® solution containing 1 g/l nitrite base inhibitor during immersion time

Figure 6: Nyquist representation of the electrochemical impedance plots for carbon steel alloy in the SULFIRAN® solution containing phosphate base inhibitor during immersion time

As it is shown in the plots, their semi-circular shape is an indication of the activation-controlled nature of reactions with a single charge transfer process. The diameter of the semi-circle gives the polarization resistance \( R_p \), which is inversely proportional to the corrosion rate. It seems that the protecting film formation is completed after 2 hours for nitrite and phosphate base inhibitors and the corrosion inhibition becomes optimum at this time. The equivalent circuit obtained from the simulated EIS curves is shown in Figure 7. The equivalent circuit consists of the solution resistance \( R_s \), the polarization resistance \( R_p \), and the constant phase element (CPE).

Figure 7: Equivalent electrical circuit to model EIS data for carbon steel alloy in the SULFIRAN® solution containing different inhibitors

A generalized CPE describes the non-ideal behavior of the capacitance. The impedance of CPE is given by Equation 11 [5].

\[
Z_{CPE} = [Q(j\omega^n)]^{-1} \tag{11}
\]

where, \( j \) is the imaginary number and \( Q \) stands for a frequency-independent constant; \( \omega = 2\pi f \) is the angular frequency (rad/s) and \( f \) represents the frequency of the applied signal; \( n \) is the CPE exponent. There are different factors affecting the CPE element in equivalent circuits such as the surface roughness, a distribution of reaction rates, varying thickness or composition, and non-uniform current distribution [6-10]. The simulation results are demonstrated in Tables 2 and 3. It must be noted that all of the studied systems give \( n \) values of approximately equal to unity, indicating the predominant effect of capacitive behavior. It is observed that the value of CPE decreases, while the value of \( R_p \) increases by increasing time.

The results obtained from the lab measurements show that the flow does not affect the corrosion inhibition of nitrite base inhibitor. The polarization curves are shown in Figure 8 for the carbon steel in the presence of 1 g/l nitrite base inhibitor with and...
without a rotating disc electrode (RDE). The rotation rate was 3000 rpm. It is clear that the corrosion rates are equal to each other. However, corrosion potential shifts towards more positive values with rotation electrode.

**Table 2: Optimum values of impedance parameters for carbon steel alloy in the SULFIRAN® solution containing nitrite base inhibitor during immersion time**

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>$R_p$ (Ωcm²)</th>
<th>CPE element $Y_0$ (Ω⁻¹ cm² sec⁻¹)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1211</td>
<td>3.2E-4</td>
<td>0.8819</td>
</tr>
<tr>
<td>1 hour</td>
<td>1830</td>
<td>2.64E-4</td>
<td>0.9010</td>
</tr>
<tr>
<td>2 hours</td>
<td>1865</td>
<td>2.62E-4</td>
<td>0.8997</td>
</tr>
<tr>
<td>20 hours</td>
<td>5815</td>
<td>2.1E-4</td>
<td>0.9271</td>
</tr>
</tbody>
</table>

**Table 3: Optimum values of impedance parameters for carbon steel alloy in the SULFIRAN® solution containing phosphate base inhibitor during immersion time**

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>$R_p$ (Ωcm²)</th>
<th>CPE element $Y_0$ (Ω⁻¹ cm² sec⁻¹)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>943</td>
<td>4.2E-4</td>
<td>0.8989</td>
</tr>
<tr>
<td>1 hour</td>
<td>1076</td>
<td>3.7E-4</td>
<td>0.9075</td>
</tr>
<tr>
<td>2 hours</td>
<td>1252</td>
<td>3.5E-4</td>
<td>0.9091</td>
</tr>
<tr>
<td>20 hours</td>
<td>4243</td>
<td>3.1E-4</td>
<td>0.9080</td>
</tr>
</tbody>
</table>

The weight loss measurements results in the presence of 5 w/w% phosphate base inhibitor through pilot tests are shown in Table 4. It is found that the corrosion rate is not satisfactorily in the oxidizer tower. Therefore, the phosphate base inhibitor cannot be a good candidate for this process. On the other hand, on line corrosion monitoring by linear polarization resistance (LPR) technique through the pilot test showed that the corrosion rate of carbon steel was 5±0.3 mpy in the absorption tower. This result confirms the weight loss measurements.
resistance (LPR) technique through the pilot test showed that the corrosion rate of carbon steel alloy was less than 1 mpy.

CONCLUSIONS
The inhibitive effects of nitrite- and phosphate-based inhibitors on carbon steel alloy samples in a Fe-EDTA solution used in the acid gas treatment process (the SULFIRAN® solution) were investigated. The results indicated that adding these inhibitors reduced the corrosion rate to a suitable value (<5 mpy). For both inhibitors, the inhibition efficiency increased with the concentration of inhibitors. The inhibition efficiency for phosphate base inhibitor was found to be less than the nitrite base inhibitor.

ACKNOWLEDGEMENTS
We gratefully acknowledge the support for this work by National Iranian Oil Company (NIOC). The authors wish to thank Dr H. R. Faridi for reviewing this paper.

REFERENCES