Corrosion Inhibition of Carbon Steel in SULFIRAN® Process

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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 H_2S from gas streams [1-3]:

1) Liquid and solid H_2S 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% H_2S removal efficiency. In the SULFIRAN® process, the iron chelate solution, which is used as a catalyst for H_2S removal, has been licensed by RIPI. This process is highly flexible and can be used for a wide variety of H_2S 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 H_2S catalyst contact area (absorber) and the catalyst regeneration area (oxidizer). In initial steps, the ionized H_2S is converted to elemental Sulfur. The ionization steps are as follows:

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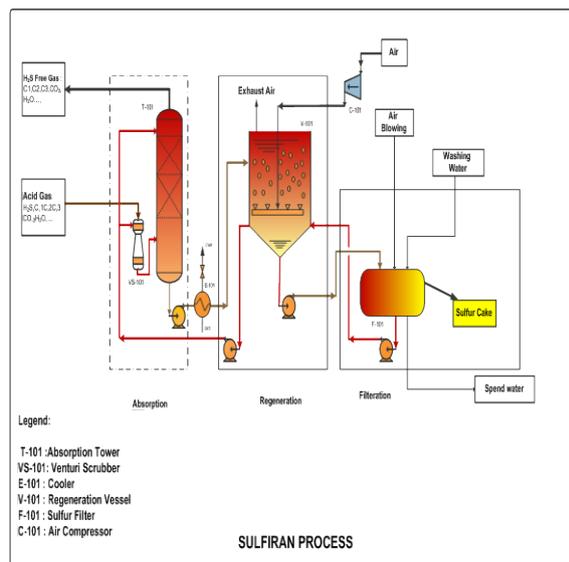
Figure 1: A schematic of the SULFIRAN® process

$$H_2S(gas) + H_2O(aq) \rightleftarrows H_2S(aq) + H_2O(aq) \qquad (1)$$

Then, the H_2S ionizes to bisulfide (HS^-).

$$H_2S(aq) \rightleftarrows HS^-(aq) + H^+(aq) \qquad (2)$$
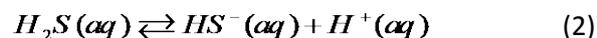
Based on Figure 1, in the absorption section (T-101), bisulfide is oxidized to sulfur by reducing the ferric ions (Fe^{3+}) to ferrous state (Fe^{2+}) as shown below (Equation 3):

$$HS^-(aq) + 2Fe^{3+}(aq) \rightarrow S(Solid) + 2Fe^{2+}(aq) + H^+(aq) \quad (3)$$

The upstream from T-101 is H_2S-free gas. The downstream is a mixture of chelate solution with suspended sulfur, which goes to chelate cooler (E-101) because the temperature of the catalyst must not exceed 40 $^{\circ}$C due to catalyst degradation; then, it will go to oxidizer vessel (V-101). In the oxidizer vessel, atmospheric oxygen will be absorbed into the catalyst solution.

$$\frac{1}{2}O_2 + H_2O \rightleftarrows \frac{1}{2}O_2(aq) + H_2O(aq) \qquad (4)$$
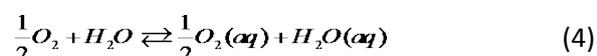
Next, the ferrous irons will be re-oxidized to ferric ions and the catalyst will be regenerated.

$$\frac{1}{2}O_2(aq) + H_2O(aq) + Fe^{2+}(aq) \rightarrow 2OH^-(aq) + H^+(aq) + Fe^{3+} \quad (5)$$
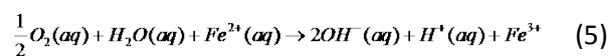
Now, the regenerated catalyst is ready for use in the absorber section again. The overall reaction is shown in Equation 6.

$$H_2S + \frac{1}{2}O_2 \rightarrow H_2O + S \qquad (6)$$
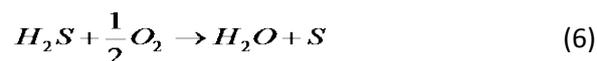
In this work, the corrosion inhibition of carbon steel alloy in SULFIRAN® solution in the presence of nitrite and phosphate base inhibitors was investigated by using lab and pilot tests.

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

$$IE\% = \frac{WL - WL_i}{WL} \times 100 \qquad (7)$$

where, WL_i and WL 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 cm^2 and 36 cm^2 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 CO_2 (98.4 v/v%)/H_2S (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 10^4 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.
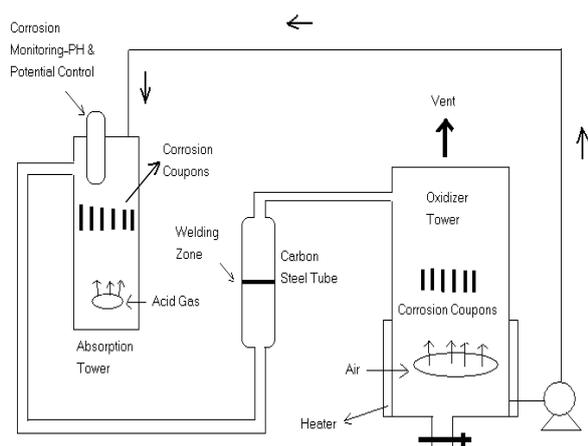

Figure 2: A schematic of pilot plant

The flow rate of acid gas and catalyst solution were 300 ml.min^{-1} and 2.5 l.min^{-1} respectively. Potentiometric (105±15 mV vs. SCE) measurements and pH (8.5±0.5) control were used during the tests

to adjust the flow rate of acid gas in the absorption tower. On line corrosion monitoring was performed by linear polarization resistance (LPR) technique in the absorption tower too. The duration of the test was 144 hrs in the pilot test. The corrosion coupons with welded areas were put in the absorption and oxidizer towers. A small full section carbon steel tube with a height, diameter, and thickness of 15 cm, 5.3 cm, and 0.4 cm respectively was put in the line between the oxidizer and reservoir towers in the pilot plant to study flow effects. Nitrite and phosphate base inhibitors were employed in concentration ranges of 0 to 0.1 w/w% and 1 to 5 w/w% respectively.

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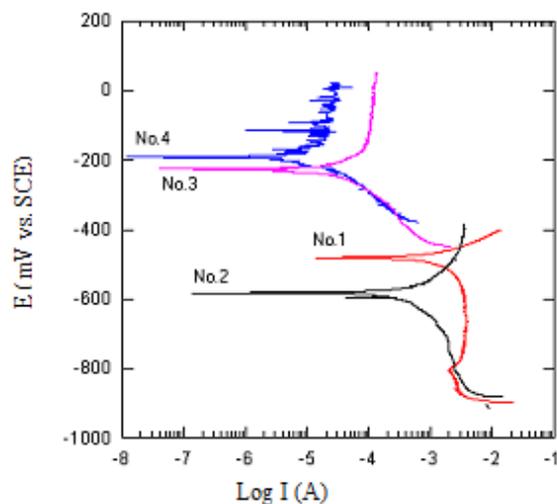
Figure 3: Potentiodynamic polarization curves of carbon steel in the SULFIRAN® solution in the presence of nitrite base inhibitor, (1) Blank, (2) 0.05 g/l, (3) 0.075 g/l, and (4) 0.1 g/l

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

blank solution (uninhibited case). The corrosion rate values decreased from 295 mpy for the blank solution to 1.5 mpy and 1.19 mpy respectively by adding 0.1% of nitrite base and 5% phosphate base with the corresponding inhibition efficiency of 99.46 and 99.6. The anodic branches shifted more than cathodic branches in the presence of inhibitors. It means that these inhibitors act through an anodic mechanism.
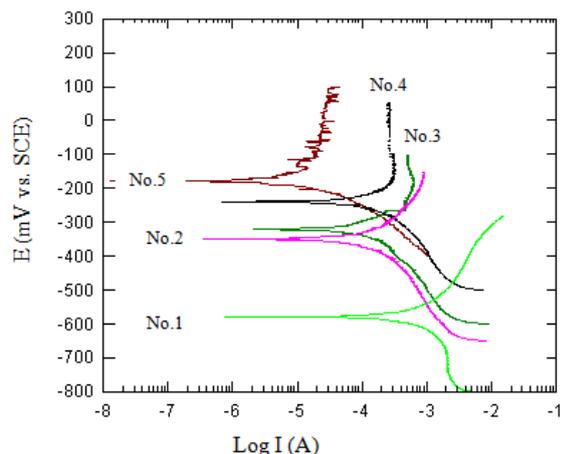

Figure 4: Potentiodynamic polarization curves of carbon steel in the SULFIRAN® solution in the presence of phosphate base inhibitor, (1) 1 wt.%, (2) 2 wt.%, (3) 3 wt.%, (4) 4 wt.%, and (5) 5 wt.%

It is found that the protective oxide film is formed in the presence of nitrite according to the following reaction [4].

$$4Fe + 3NO_2^- + 3H^+ \rightarrow 2\gamma Fe_2O_3 + NH_3 + N_2 \quad (8)$$
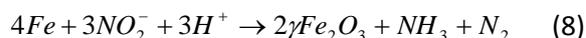
In addition, phosphates show corrosion inhibition behavior in the presence of oxygen. The dissolved oxygen in the system oxidized iron to form γFe_2O_3 and caused the discontinuities in the oxide film to be filled by ferric phosphate [4].

$$Fe^{2+} + H_2PO_4^- \rightarrow FeH_2PO_4^+ \quad (9)$$

$$FeH_2PO_4^+ + 2H_2O \rightarrow FePO_4 + 2H_2O + 2H^+ + e \quad (10)$$
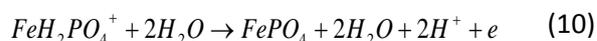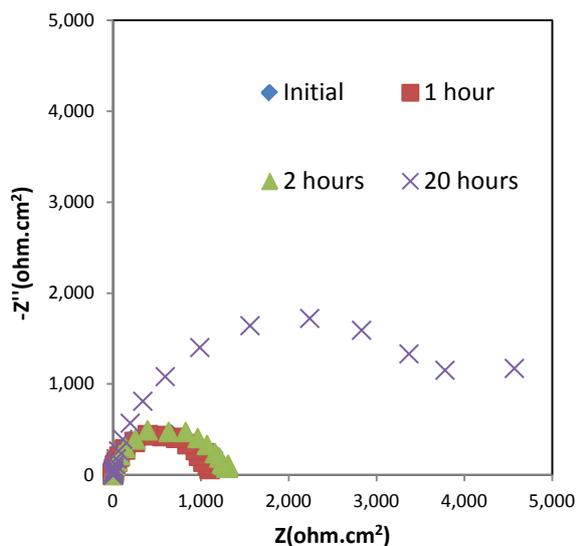
The Nyquist representation of the electrochemical impedance plots for carbon steel samples in the SULFIRAN® solution containing nitrite and phosphate base inhibitors during the immersion time are presented in Figures 5 and 6 respectively.

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

| Concentration of Inhibitor (w/w%)	E_{corr} (mV vs. SCE)	b_a (mV/dec)	b_c (mV/dec)	C.R (mpy)	IE (%)
Blank	-483.5	113	1281	295	-
Nitrite base					
0.05	-584.6	125	276	42.6	85.56
0.075	-229	126	161	3.6	98.78
0.1	-192	111	62	1.5	99.49
Phosphate base					
1	-578	248	237	95.5	67.63
2	-349	213	267	17.59	94.04
3	-237	100	100	11.84	95.99
4	-320	115	221	15.5	94.74
5	-179	638	94	1.19	99.6
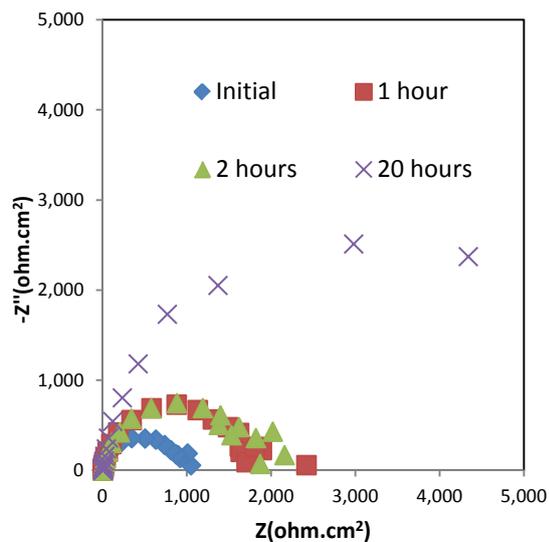
Figure 5: Nyquist representation of the electro-chemical impedance plots for carbon steel alloy in the SULFIRAN® solution containing 1 g/l nitrite base inhibitor during immersion time

Figure 6: Nyquist representation of the electro-chemical 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).
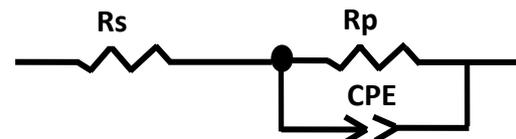
Figure 7: Equivalent electrical circuit to model EIS data for carbon steel alloy in the SULFIRAN® solution containing different inhibitors

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

Time	R_p (Ωcm^2)	CPE element	
(days)		Y_0 (Ω^{-1}cm^{-2}sec^n)	n
Initial	1211	3.2E-4	0.8819
1 hour	1830	2.64E-4	0.9010
2 hours	1865	2.62E-4	0.8997
20 hours	5815	2.1E-4	0.9271

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

Time	R_p (Ωcm^2)	CPE element	
(days)		Y_0 (Ω^{-1}cm^{-2}sec^n)	n
Initial	943	4.2E-4	0.8989
1 hour	1076	3.7E-4	0.9075
2 hours	1252	3.5E-4	0.9091
20 hours	4243	3.1E-4	0.9080

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.
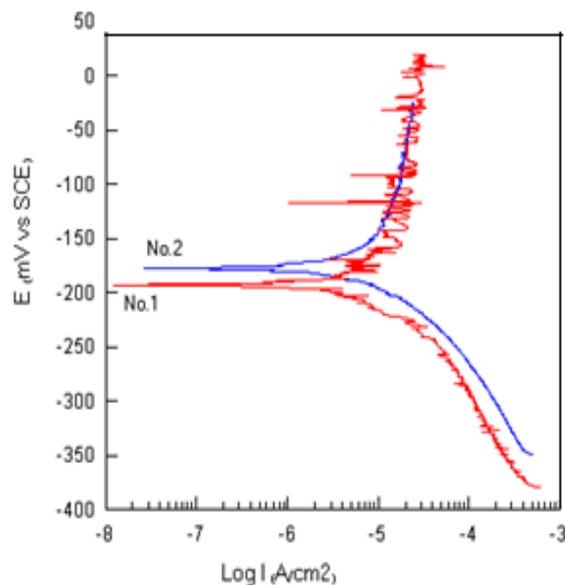
Figure 8: Potentiodynamic polarization curves of carbon steel in the SULFIRAN® solution in the presence of nitrite base inhibitor (1 g/l), (1) without rotation and (2) with a rotating disc electrode (3000 rpm)

Table 4: The results of weight loss obtained from the pilot test for carbon steel alloy in the SULFIRAN® solution

Column	Average Corrosion Rate (mpy)
Absorption	6.2
Oxidizer	68.24

The results obtained from the weight loss measurements in the presence of 1 w/w% nitrite base inhibitor through the pilot tests are shown in Table 5.

Table 5: The results of weight loss obtained from the pilot test for carbon steel alloy in the SULFIRAN® solution containing 1 w/w% nitrite base inhibitor

Column	Average Corrosion Rate(mpy)
Absorption	0.74
Oxidizer	0.27

It is found that the corrosion rates are in acceptable ranges in the oxidizer tower and in the absorption tower. 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 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

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