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Screening of an Environmentally Friendly Corrosion Inhibitor for Mildly Acidic Geothermal Fluid Applications

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ABSTRACT

Successful utilization of mildly acidic well fluids where the acidity is derived from sulfur species has been demonstrated through downhole pH adjustment. Limitations on this method of corrosion control have been encountered through high temperature precipitation of anhydrite requiring close balance of pH for minimization of anhydrite and control of corrosion. This constraint has discouraged the use of NaOH for corrosion control in some geothermal wells. An alternative scenario using corrosion inhibitors, with or without some intermediate pH adjustment has been proposed but has found resistance from users concerned with environmental impact of traditional oil and gas field inhibitors. This paper provides laboratory screening results for an environmentally friendly candidate corrosion inhibitor for acidic geothermal fluids. The candidate inhibitor was found to meet the requirements for inhibition in pH 3.5 brine but also did not adversely impact on the protective properties of H_2S at higher pH values of 4.5 and 6.0. The results provide encouragement for use of this alternative solution for production of geothermal wells cased in carbon and low alloy steels that encounter mildly acidic fluids after completion.

1. INTRODUCTION

Many geothermal wells that are cased in low-carbon steels encounter acidic well fluids which can benefit from the application of pH control chemicals such as NaOH, however, at high temperatures the injection of NaOH can result in rapid scaling by one or more of Calcite, Silica and Anhydrite scales. Additional complications encountered with acid wells include the reductive deposition of heavy metals on freely corroding steel that can result in galvanic corrosion and changes in production fluid pH levels that require frequent adjustment of the NaOH addition. Corrosion inhibitors have been proposed as an alternative to pH adjustment in mildly acidic geothermal wells. The use of corrosion inhibitors is one of the most cost-effective and practical methods of corrosion protection. The employment of an appropriate inhibitor can allow the production of wells cased in carbon steels that encounter acidic fluids without pH adjustment. Inhibitors can also be used to allow wells in acidic reservoirs to be cased in lower-grade carbon steels, which significantly reduce the costs compared with the use of high-grade alloys in the same project. However, not all corrosion inhibitors are environmentally friendly. Many corrosion inhibitors contain inorganic, organic and polymeric compounds that are toxic to animal and/or plant life and do not fulfill completely the requirements imposed by environmental protection standards.

The objective of the research was to study the effect of environmentally friendly corrosion inhibitor, Solenis Amercor NAF on corrosion control of K55 casing material in simulated test electrolyte containing 9,500 mg/kg Cl ion and 5×10^{-5} mol/kg H_2S at 80°C and atmospheric pressure using a rotating cylinder electrode (RCE) technique in our laboratory. The long-term objective of this work was to test this inhibitor in a pressure vessel test at higher pressure and temperatures before testing in an actual geothermal field. This paper give a summary of the results from screening test at 80°C and atmospheric pressure using RCE.

2. EXPERIMENTAL PROCEDURE

A rotating cylinder electrode (RCE) and a one liter cell with water jacket and drain valve were used to test the effect of Solenis Amercor NAF environmentally friendly inhibitor on corrosion of K55 casing materials samples provided by Tenaris NKK Tubes, with the following chemical composition (in wt%): C 0.5 and Mn 0.9.

The test electrolyte used was comprised of ultra-pure water with 9,500 ppm of chloride ions added in the ratio 1:5:0.5 of potassium, sodium and calcium chloride typical of some geothermal wells in Japan. Sodium sulfide (6×10^{-3} g/L) was added to the conditioned test solution with the aim of achieving a low partial pressure of H_2S in the cell, again similar to that encountered in some typical geothermal wells in Japan. The pH of the electrolyte was adjusted by the addition of small amounts of 0.5 M solution of sulfuric acid (H_2SO_4) or 0.5 M sodium hydroxide (NaOH). The electrolyte solution was studied at pH of 3.5, 4.5 and 6.0.

The appropriate test electrolyte was added to the RCE cell for each test and a heated water solution was circulated around the cell to maintain an average temperature of 80°C for the entire test run. Oxygen-free environment was achieved by bubbling high purity nitrogen gas for one hour prior to testing. Purging was then maintained at a high rate until the experiment had concluded. A rotation speed of 200 rpm was used for all experiments.

All electrochemical measurements were obtained by using a PGZ 100 potentiostat (Radiometer 115 Analytical) and an EG&G Model 273A potentiostat (Princeton Applied Research). The counter electrode was constructed from graphite, while the reference electrode was a saturated calomel electrode (SCE). The working electrodes were cylinders of Tenaris NKK K55 casing steel (15mm diameter). The electrodes were surface ground to a final 800 grit emery paper then washed with distilled water and ethanol prior to beginning the RCE test. The electrodes had a surface area of 3 cm^2 and this value was used throughout for corrosion rate calculations. Each working electrode was mounted on a Teflon sleeve, attached to an EG&G PARC rotator. Potentiodynamic scans were conducted after a 3600s delay at the open circuit potential (OCP), and from the OCP in the cathodic and anodic directions, respectively, at a scan rate of 1 mV/s.

At each pH, a first test was run with no inhibitor addition in order to determine the baseline corrosion rate for that test solution. Inhibitor was evaluated at four different concentrations (20, 40, 60 and 200 mg/kg), sequentially added into the same electrolyte. For each test, a new sample was prepared according to the above-mentioned surface preparation.

Appendix A provides a Fe-H_2S-H_2O Pourbaix diagram for this system.

3. RESULTS

3.1 Open Circuit Potential (OCP)

Figure 1 shows OCP measurements results K55 material vs. pH of experimental solutions at different inhibitor concentrations, recorded after 3,600s at 80 °C.

The results showed that generally by increasing the pH of the solution from 3.5 to 6, the potential was shifted to more negative values which is in accord with the Pourbaix diagram prepared for the 80 ºC. Because the brine had a small amount of dissolved H_2S reducing conditions were assumed and it was asserted that the corrosion reaction should sit at or near the hydrogen stability line. For example, in the case of using no inhibitor, OCP shifted toward the negative potentials following the slope of the hydrogen stability line, changing from -743 mV vs. SCE (-499 mV vs. SHE) to -864mV vs SCE (-620 mV vs. SHE) by increasing the pH from 3.5 to 6.0.

In addition, at each tested pH value, OCP potentials were generally shifted to more positive potentials by increasing the inhibitor concentration, although some exceptions were observed.

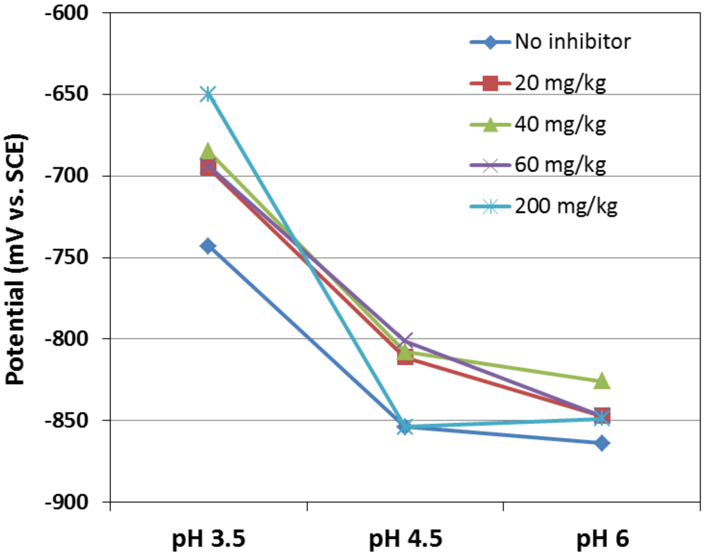

Figure 1: OCP for K55 casing material as a function of pH for different inhibitor concentrations at 80 °C after 3,600s.

3.2 Corrosion Current

Figure 2, Figure 3 and Figure 4 show the effect of inhibitor concentration on potentiodynamic scans for K55 casing material in the experimental solution at pH 3.5, 4.5 and 6.0, respectively. These scans are plotted using the convention described in ASTM G3-2014 where the potential is varied, and the corrosion current density required to move the potential away from the corrosion potential is measured. By convention the negative current is plotted in the positive direction and the characteristic slopes of these curves (the anodic and cathodic Tafel slopes) are used to graphically estimate the corrosion current density (i_{corr}) at the OCP. The i_{corr}, corrosion potential and corrosion rate (CR) estimates are summarized in Table 1.

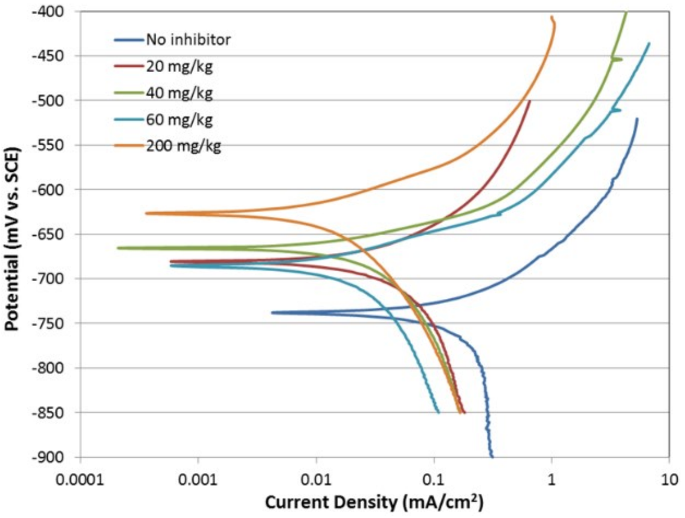

Figure 2: Effect of inhibitor concentration on potentiodynamic curves for K55 electrodes at pH 3.5, and 80°C.

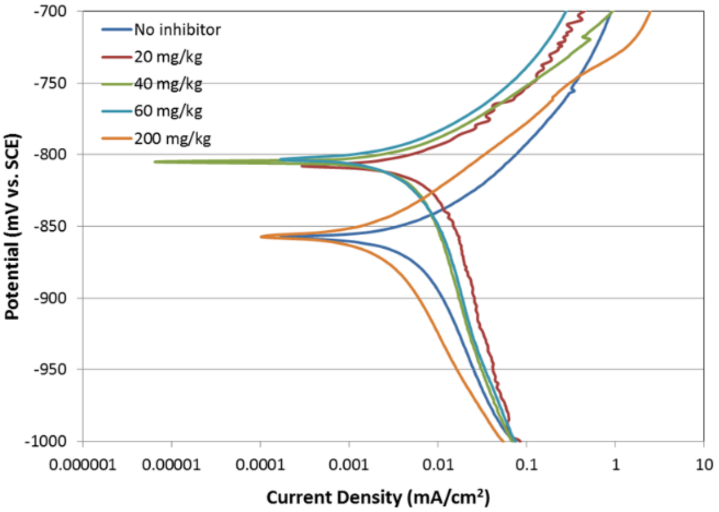

Figure 3: Effect of inhibitor concentration on potentiodynamic curves for K55 electrodes at pH 4.5, and 80°C.

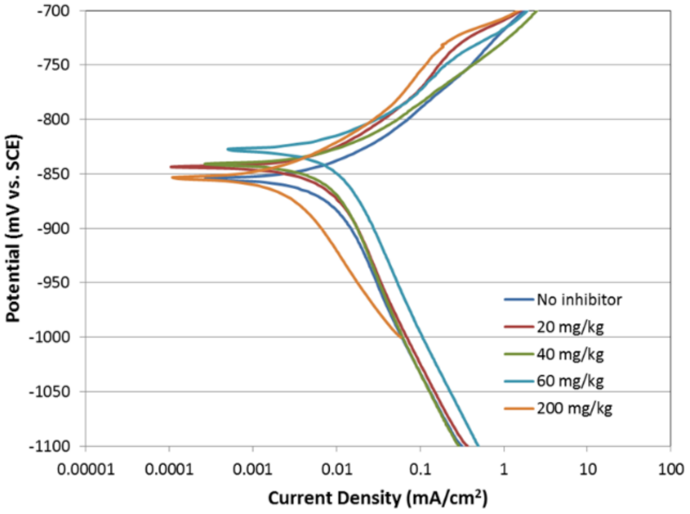

Figure 4: Effect of inhibitor concentration on potentiodynamic curves for K55 electrodes at pH 6.0, and 80°C.

The results given in Figures 2 through 4 and Table 1 show that:

- Polarization tests showed decreasing corrosion rate trends at pH 3.5 and 4.5. By increasing the inhibitor concentration, the corrosion rates decreased, and higher inhibition percentages were achieved. The maximum inhibition percentages obtained at 200 ml/l inhibitor concentration at pH 3.5 and 4.5 were between 93% and 79%, respectively.
- At pH 6.0, the trend observed between the inhibitor concentration and corrosion inhibition percentage was not definitive. The corrosion rate was decreased about 17% by adding 20 mg/kg of inhibitor. However, the corrosion rate was increased by adding more inhibitor up to 200 mg/kg.
- It can be seen from the Pourbaix diagram (Appendix A) that raising the pH will increase the stability of iron sulfide deposition on the working electrode to give a protective corrosion product and subsequently decrease the corrosion rate as was observed for 0 inhibitor addition. However, at pH 3.5 and 4.5, greatest corrosion inhibition was observed at the highest inhibitor concentration tested at 200 mg/kg, 93% and 79% inhibition being achieved at pH 3.5 and 4.5, respectively. At high tested pH 6.0, results were not definitive. Corrosion current density was decreasing and accelerating intermittently by increasing the corrosion inhibitor concentration. This behavior and also inhibition mechanism are not well understood at this stage, but it is possible that the inhibition mechanism on the working electrode at high pH 6.0 was interfering with deposition of iron sulfide.

Table 1 Results from the polarisation scans for K55 materials at pH 3.5, 4.5 and 6.0, with different inhibitor concentration in test electrolyte.

pH	Inhibitor concentration (mg/kg)	Corrosion potential (mV vs SCE)	Corrosion Current density (μA/cm^2)	Polarization resistance (Ω.cm^2)	Ba (mV/decade)	Bc (mV/decade)	Corrosion rate (mm/year)	Inhibition %
3.5	0	-743	96.89	131	61.0	-121.5	1.124	0.0
	20	-685	20.43	536	59.5	-81.4	0.237	78.9
	40	-670	9.84	633	29.3	-52.2	0.114	89.8
	60	-690	7.79	891	34.2	-57.5	0.094	91.6
	200	-631	6.62	1300	42.2	-67.3	0.077	93.1
4.5	0	-882.7	7.83	1670	41.8	-143.2	0.091	0.0
	20	-812	6.94	1820	47.4	-122.3	0.081	10.9
	40	-810	4.08	2730	37.1	-116.9	0.047	48.3
	60	-808	3.36	3180	38.4	-94.1	0.039	57.1
	200	-861	1.59	5780	41.8	-71.1	0.019	79.1
6.0	0	-860	5.07	2240	45.4	-96.2	0.059	0.0
	20	-848	4.22	2350	46.1	-80	0.049	16.9
	40	-845	5.29	2080	40.6	-103.2	0.061	-3.4
	60	-831	4.84	1720	36.0	-71.7	0.056	5.1
	200	-815	8.07	1480	37.9	-131.6	0.094	-59.3

3.3 Inhibitor processes

Figure 5 and Figure 6 summaries the effect of inhibitor concentration on inhibition percentage and corrosion potential at different pH values.

Figure 5 illustrates that at the lower tested pH values (e.g. 3.5 and 4.5) adding inhibitor up to 60 mg/kg to the test solutions had a significant effect on corrosion mitigation. However, more inhibitor dosage had less pronounced effect on corrosion inhibition.

Figure 6 shows that at pH 3.5, the corrosion potential generally shifted toward the positive direction with increasing the corrosion inhibitor concentration. However, at higher pH values, corrosion potentials did not change significantly as the corrosion inhibitor concentration was changed. The corrosion potential shifted to more negative potential by increasing the pH value from 3.5 to 4.5, however, no significant difference was observed as the pH was increased from 4.5 to 6.0. This was consistent with the initial OCP results reported in Figure 1.

Displacement of corrosion potential on addition of the inhibitor is often a useful indication of which one of anodic or cathodic processes is being retarded. In the case of anodic control, displacement of corrosion potential in the positive direction would indicate retardation of anodic process and mean that an anodic control process was active. In contrast, displacement of corrosion potential in the negative direction would indicate retardation of the cathodic process and that a cathodic control process was being used.

At pH 3.5, the corrosion potential shifted in the positive direction which would indicate an anodic control process was active. However, little change in corrosion potential was observed at higher pH (eg. 4.5 and 6.0) and this suggests that both anodic and cathodic processes were being retarded, Dariva et al. (2014).

In addition, results showed that the anodic slopes were almost similar for all inhibitor concentrations tested at all pH values tested, see Table 1. However, the cathodic slope was seen to be changing. Displacement of the polarization curve without a change in Tafel slope in the presence of the inhibitor indicates that the adsorbed inhibitor acts by blocking active sites, rather than by affecting the mechanism of reaction. An increase of cathodic Tafel slope due to the inhibitor would indicate that the inhibitor may act by affecting the mechanism of reaction, Shreir st al. (1994). In the case of this tested inhibitor, the results are more complicated as the cathodic slope has changed while the anodic slope remained almost unchanged. This could be related to the fact that anodic and cathodic processes may be inhibited differently by this inhibitor.

It is often not possible to assign a single general mechanism of action to an inhibitor, because the mechanism may change with experimental conditions. Thus, the predominant mechanism of action of an inhibitor may vary with factors such as its concentration, the pH of the solution, the nature of the anion of the acid and the presence of other species in the solution, Shreir st al. (1994). If blocking of the anodic reaction sites was the predominant mechanism of corrosion inhibition for the tested inhibitor, then the inhibitor concentration would be important to ensure that the full coverage of anion sites was happening.

In the case of the tested inhibitor, it is clear that the inhibition mechanism is dependent on pH of the H_2S containing solution. At low pH 3.5, it seems that the iron sulfide corrosion products are not stable at the working electrode surface and so iron sulfide formation does not interact with the inhibition mechanism. However, as it is predicted by the Pourbaix diagram (Appendix A), raising the pH will increase the stability of iron sulfide deposition on the working electrode and normally this would result in protection of the underlying steel. However, it appears that the inhibition mechanism was interfering with the corrosion product stability. Therefore, the inhibition percentage was decreased 16% by increasing the pH from 3.5 to 4.5 and at high pH 6.0, the results were not definitive.

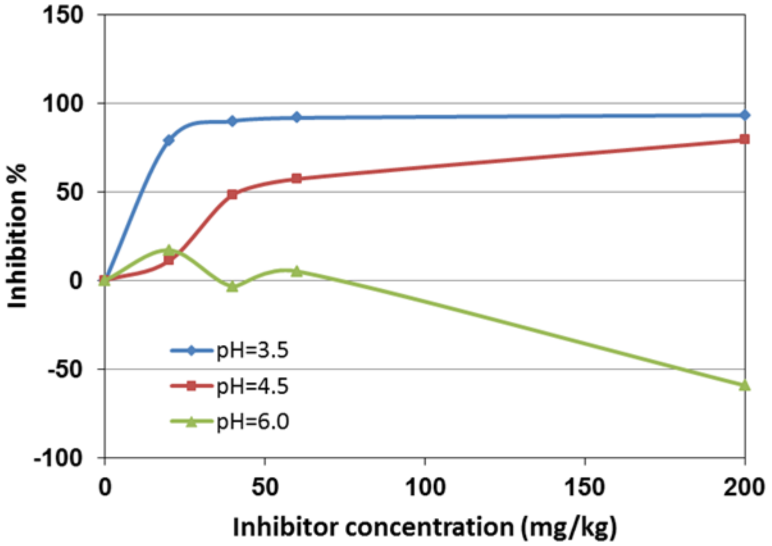

Figure 5: Effect of inhibitor concentration on inhibition percentage for K55 electrodes at different pH values.

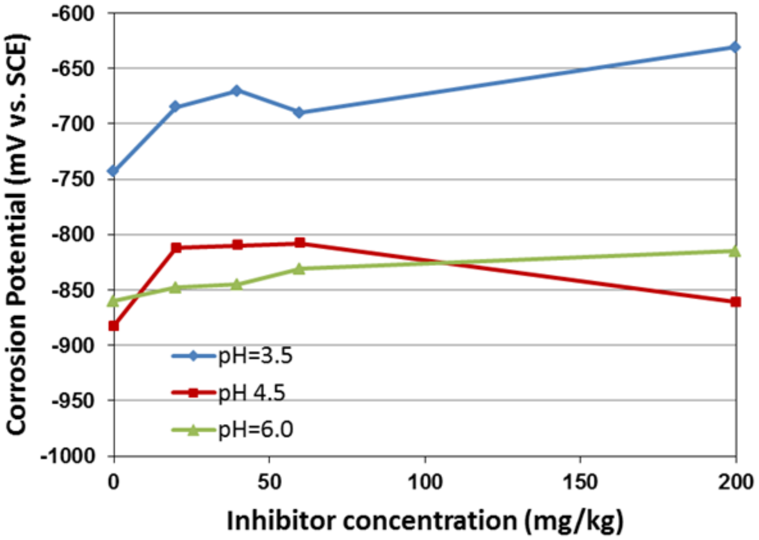

Figure 6: Effect of inhibitor concentration on corrosion potential for K55 electrodes at different pH values. Note: Corrosion potentials derived from potentiodynamic curves in Figures 2-4.

4. CONCLUSION

An environmentally friendly corrosion inhibitor from Solenis (Amercor NAF) was used to study corrosion mitigation of K55 casing material in simulated acidic geothermal electrolyte containing 9,500 mg/kg chloride ions and 5×10^{-5} mol/kg H_2S at 80 °C at different pH values of 3.5, 4.5 and 6.0 using a spinning disc electrode. Results showed a decrease in corrosion rate as a function of increasing pH without inhibitor addition. Polarization tests showed decreasing corrosion rate trends at pH 3.5 and 4.5 with increasing inhibitor addition. Inhibitor concentrations up to 200 mg/kg were used, the corrosion rates showed continuous decrease up to this level where the highest inhibition percentages were achieved. Even at pH 6.0 the greatest corrosion inhibition was observed at the highest inhibitor concentration tested at 200 mg/kg. 93% and 79% of inhibition was achieved at pH 3.5 and 4.5, respectively. However, at pH 6.0, the trend observed between the inhibitor concentration and corrosion inhibition percentage was not definitive.

It is believed that the inhibition mechanism is dependent on pH of the H_2S containing solution. At the lowest pH tested of 3.5, it seems that the iron sulfide corrosion products were not stable at the working electrode surface and in the absence of these corrosion products there is no interaction between corrosion products and the inhibitor. However, at pH 6.0 stable iron sulfides are predicted to form by the Pourbaix diagram, raising the pH will increase the stability of iron sulfides that are depositing on the working electrode and it seems that these iron sulfides were interfering with the inhibition mechanism. Therefore, the inhibition percentage was decreased 16% by increasing the pH from 3.5 to 4.5 and at high pH 6.0, the results were less definitive.

5. REFERENCES

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6. ACKNOWLEDGEMENT

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APPENDIX A : POURBAIX DIAGRAM

A-1: Pourbaix diagram for Corrosion Test Loop Conditions at 80oC, Total S=5×10^{-5} mol/kg, Total Fe=1×10^{-6} mol/kg. Line (a) for p(H_2)=1 bar