Evaluation of Corrosion Inhibitors for Acidic Geothermal Wells

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ABSTRACT

As enhanced geothermal systems (EGS) grows so too is the need for dealing with acid brines. Already in Indonesia, Philippines, Turkey, Japan and Europe some plants cannot utilize their geothermal resources due to the acidity and aggressiveness of the brine. Geothermal wells can be sometimes acidic due to high levels of carbon dioxide (CO_2) and hydrogen sulfide (H_2S). Often the pH can drop to 5, and in some cases to 3, under these conditions. This acidic, often saline, water is very corrosive. This led to the investigation of corrosion inhibitors under these highly aggressive conditions in order to assist the wider use of existing and future acidic geothermal resources.

Corrosion inhibitors were evaluated in a series of screening tests. Initial screening was conducting using 5 minute visual tests at room temperature. This process quickly eliminated a number of obviously poor inhibitors. Next, jar test screening was conducted for 18 hours at pH 7 and 95 ^{o}C. This further reduced the number of acceptable inhibitors. Finally the leading candidates were evaluated at acidic pH. The promising inhibitors were also evaluated using several electrochemical techniques.

1. Introduction

Geothermal plants use heated water and/or steam to the generate power. For most plants, this water is typically contaminated with corrosive impurities. Dissolved ions such as chloride and sulfate can be present in high levels to form salty brines. In some areas, the total dissolved solids can exceed 100,000 ppm. Chloride and sulfate are known to be very aggressive towards iron so these brines tend to have high levels of corrosion.(Drew, 1994)

Dissolved gasses such as carbon dioxide, CO_2, and hydrogen sulfide, H_2S, are often present as well. These gasses can lower the pH, creating very aggressive water. When it dissolves in water, carbon dioxide can react to form carbonic acid according to equation 1. This has the effect of lowering the pH. It's not unusual to have water around pH 5 when carbon dioxide is present.(Haizlip et al., 2016)

$$\text{(eq 1)} \quad CO_{2\,(g)} + H_2O_{(l)} \longrightarrow H_2CO_{3\,(aq)}$$

In certain areas it's even possible to have hydrochloric acid (HCl), or bisulfuric acid (HSO_4^-) present.(Lichti et al., 2010) These acids are produced from the dissolved rock in the geothermal well. Since both hydrochloric and bisulfuric acid are strong acids, they can dissolve the iron in the steel and eat away at well casings and any other exposed metal in which they come in contact with. This can lead to catastrophic failure and well shutdown in extreme cases.

Due to these aggressive conditions, there is a need for an inhibitor to help mitigate corrosion. In this study, a series of tests were initiated to evaluate potential corrosion inhibitors. Initial tests were conducted at pH 7 to screen out poor inhibitors. Follow-up tests were conducted at pH 5 to remove additional poorly performing inhibitors. Finally, tests were conducted at pH 5 under a CO_2 atmosphere.

2. Experimental Section

2.1 Five min screening

Coupons were exposed to the brine in Table 1 for five minutes. The coupons were evaluated visually. High levels of corrosion led to coupons which were black due to the formation of iron sulfide. Corrosion inhibitors were evaluated on a subjective scale. Only inhibitors which passed or had mixed results were evaluated further

Pass: Little or no visual corrosion. Coupon was mostly or completely grey.

Mixed: Black or brown spots visible on the edge of the coupon.

Fail: Coupon was brown or black throughout.

Table 1. Brine used for corrosion tests at pH 7.4.

Ion	Concentration
Cl^-	2000 ppm
SO_4^{2-}	40 ppm
Ca^{2+}	7 ppm
S^{2-}	25 ppm
HCO_3^{2-}	500 ppm
pH	7.4

Brine was created by mixing $CaCl_2$-2(H_2O), NaCl, Na_2SO_4-10(H_2O), Na_2S (60%) with deionized water. Depending on the experiment, pH was adjusted to either 7.4 or 5.0 using dilute HCl and/or NaOH in water.

2.2 Jar Tests

Secondary testing was done in sealed jars under a nitrogen atmosphere. The solutions were preheated to 95 ^{o}C with a nitrogen stream for 30 minutes. Sodium hydrosulfite was added to scavenge any remaining oxygen. Two C1010 steel coupons were attached to an alumina screw and held in place with alumina washers and nuts and submerged in the solution. The solutions were heated under a nitrogen blanket for 20 hours. The solutions were lightly stirred with a magnetic stir bar. After 20 hours, the coupons were evaluated visually and the corrosion rate was calculated by weight loss. The results are presented in mils per year (mpy).

2.3 Potentiostat

All electrochemical evaluations were performed using a Gamry MultEchem Series G 300 potentiostat. The reference electrode was a Ag/AgCl electrode and the auxiliary electrode was a graphite rod. The working electrode was a C1018 steel cylinder with a surface area of 3 cm^2 which was held in place using Teflon washers. Prior to the experiment and throughout the test gas, either air or CO_2, was purged through the solution. Experiments involving CO_2 were purged for 1 hour prior to the test to ensure an inert atmosphere. During analysis, the cylinder was rotated at 400 rpm. Linear polarization resistance (LPR) was run with a scan rate of 0.125 mV/sec with a window of +/-20 mV relative to the open circuit potential. Electrochemical impedance measurements were taken with an initial frequency of 100,000 Hz and a final frequency of 0.2 Hz. The results are plotted using Z_{real} vs. the absolute value of Z_{imag}.

3. Results and Discussion

3.1 Five Minute Screening

Inhibitors were screened by exposing coupons to geothermal brine in Table 1 for 5 minutes. This process allowed for the quick screening of a large number of inhibitors. The coupons turned dark brown or black if the inhibitor was ineffective. If the coupons remained grey then the inhibitor was deemed effective. Examples of these results are presented in Figure 1.

An example of a test which produced failing results is presented in Figure 1a. In this example, no inhibitor was used. After 5 minutes, the coupon was completely covered with dark brown or black corrosion.

An example of mixed performance is shown in Figure 1b. Amino Acid 1 provided some protection, but there is clearly some corrosion present on the edges of the coupon.

Finally, an example of passing results is shown in Figure 1c using Amine 1. The coupon was light grey with few signs of corrosion.

Figure 1. All coupons were exposed to the brine in Table 1, pH=7.4 for 5 minutes. 1a) No inhibitor - fail. 1b) Amino acid 1 - mixed. 1c) Amine 1 - pass.

A summary of the results is presented in Table 2. Carboxylic acids and amino acids were generally ineffective under these conditions with most inhibitors either failing or producing mixed results. Oximes provided some protection, with Oxime 1 passing and Oxime 2 providing mixed results. The best results were obtained with amines, imidazolines (a type of amine), and quaternary ammonium compounds (quats). Alcohol surfactants also provided good protection under these conditions. These tests narrowed down the classes of molecules for further testing.

Table 2. Summary of 5 minute screening tests.

Inhibitor	Pass/Fail
No Inhibitor	Fail
Amino Acid 1	Mixed
Amino Acid 2	Fail
Amino Acid 3	Fail
Amino Acid 4	Mixed
Oxime 1	Pass
Oxime 2	Mixed
Carboxylic acid 1	Fail
Carboxylic acid 2	Fail
Amine 1	Pass
Amine 2	Pass
Amine 3	Pass
Amine 4	Pass
Amine 5	Mixed
Amine 6	Pass
Quat 1	Pass
Quat 2	Pass
Quat 3	Pass
Thiol 1	Pass
Thiol 2	Fail
Alcohol Surfactant 1	Pass
Alcohol Surfactant 2	Mixed
Alcohol Surfactant 3	Pass
Alcohol Surfactant 4	Pass
Alcohol Surfactant 5	Pass
Imidazoline 1	Pass
Imidazoline 2	Pass
Imidazoline Quat	Pass

3.2 Jar Tests

The promising candidates from the 5-minute screening were then subjected to a more thorough jar test. Inhibitor was added at 500 ppm to the geothermal brine from Table 1. This solution was heated to 95 ^{o}C for 30 minutes under a nitrogen stream to deaerate the solution. Sodium sulfite, 500 ppm, was added to remove trace levels of oxygen. C1010 steel coupons were submerged in the solution and heated at 95 ^{o}C for 20 hours under nitrogen. Due to the higher temperature and longer exposure time, coupons were much more likely to experience corrosion in these tests. Corrosion coupons were evaluated visually and through weight loss, the results of which are summarized in Table 3.

Table 3. Evaluation of corrosion inhibitors through jar tests at 95 ºC, pH 7.4, under nitrogen.

Inhibitor	Coupon Description	Corrosion Rate
No Inhibitor	Black with deposits	9.9 mpy
Oxime 1	Black with deposits	10.2 mpy
Oxime 2	Dark grey, no deposits	10.8 mpy
Amine 1	Light grey	7.2 mpy
Amine 2	Black with deposits	5.4 mpy
Amine 3	Golden brown	7.0 mpy
Amine 4	Black with deposits	8.2 mpy
Amine 5	Light grey	5.0 mpy
Amine 6	Light grey	8.2 mpy
Amine 7	Light grey	3.9 mpy
Quat 1	Light grey	6.2 mpy
Quat 2	Light grey	7.0 mpy
Quat 3	Light grey	7.5 mpy
Thiol 1	Black with deposits	9.2 mpy
Alcohol Surfactant 1	Rusty corrosion	4.4 mpy
Alcohol Surfactant 2	Black with deposits	15.6 mpy
Alcohol Surfactant 3	Rusty corrosion	6.0 mpy
Alcohol Surfactant 4	Rusty corrosion	6.9 mpy
Alcohol Surfactant 5	Rusty corrosion	7.6 mpy
Imidazoline 1	Black with deposits	5.6 mpy
Imidazoline 2	Black with deposits	4.8 mpy
Imidazoline Quat	Light grey	3.7 mpy

There were several notable features about these tests. First, there was not a strong correlation between the appearance of the coupon and the corrosion rate. In many cases the corrosion rate was low even though the coupon was clearly corroded. The coupons which appeared uncorroded and were grey colored did not necessarily have lower corrosion rates than many of the heavily corroded coupons. This is likely due to the formation of deposits on the coupons. In several cases, black deposits formed within 10-15 minutes. These deposits can act as a physical barrier to further corrosion. The coupons with black or rust colored deposits likely had high initial corrosion rates, but lower long term corrosion rates. Since the calculated corrosion rate is the average over 18 hours, these numbers don't fully reflect the ability of the tested compounds to inhibit corrosion.

Several of these compounds did appear to provide good protection during the entire test. Quats 1-3 and the Imidazoline Quat all provided good protection. Coupons treated with these inhibitors were light grey in appearance and did not have a significant amount of visible corrosion. Also, coupons treated with amines 1 and 3 were grey in appearance. Unexpectedly, the imidazolines did not provide very good protection in these tests. The coupons treated with imidazolines had significant amounts of black deposits. The alcohol surfactants also did not provide good protection. The coupons had visible signs of corrosion within about 15 minutes and were covered with rust colored deposits following these experiments.

Table 4. Evaluation of corrosion inhibitors through jar tests at 95 ºC, pH 5.0, under nitrogen.

Inhibitor	Coupon Description	Corrosion Rate
No Inhibitor	Black with deposits	19.9 mpy
Amine 1	Dark brown	12.8 mpy
Amine 5	Light brown	6.0 mpy
Amine 7	Light brown	6.6 mpy
Imidazoline Quat	Light grey	5.2 mpy
Quat 1	Light brown	7.0 mpy
Quat 2	Light brown	5.5 mpy
Quat 3	Light brown	5.6 mpy
Alcohol Surfactant 1	Black with deposits	6.9 mpy
Alcohol Surfactant 2	Black with deposits	13.1 mpy
Imidazoline 1	Black with deposits	7.6 mpy

The most promising corrosion inhibitors were then evaluated at pH 5. Inhibitors were tested at a concentration of 500 ppm. As expected, these conditions were more aggressive and led to higher corrosion rates as seen in Table 4. Without an inhibitor, the C1010 coupons had a corrosion rate of 19.9 mpy and were covered in black deposits. All of the inhibitors tested showed some improvement compared with the control experiment. The worst performing inhibitors were Amine 1 and Alcohol Surfactant 2 which led to coupons with black deposits and corrosion rates of 12.8 and 13.1 mpy, respectively. The best result was obtained with the Imidazoline Quat, which provided very good protection. At the end of the experiment the coupons were light grey and had a corrosion rate of just 5.2 mpy. The other quaternary ammonium compounds, Quats 1,2,3 also provided good protection and had corrosion rates of 7.0, 5.5 and 5.6 mpy, respectively. At the end of the experiments, the coupons had a light brownish tint. Amines 5 and 7 were similarly effective. At the end of the runs, both sets of coupons were light brown and had corrosion rates of 6.0 and 6.6 mpy, respectively. Finally, two inhibitors, Alcohol Surfactant 1 and Imidazoline 1, both had relatively low corrosion rates of 6.9 and 7.6 mpy,

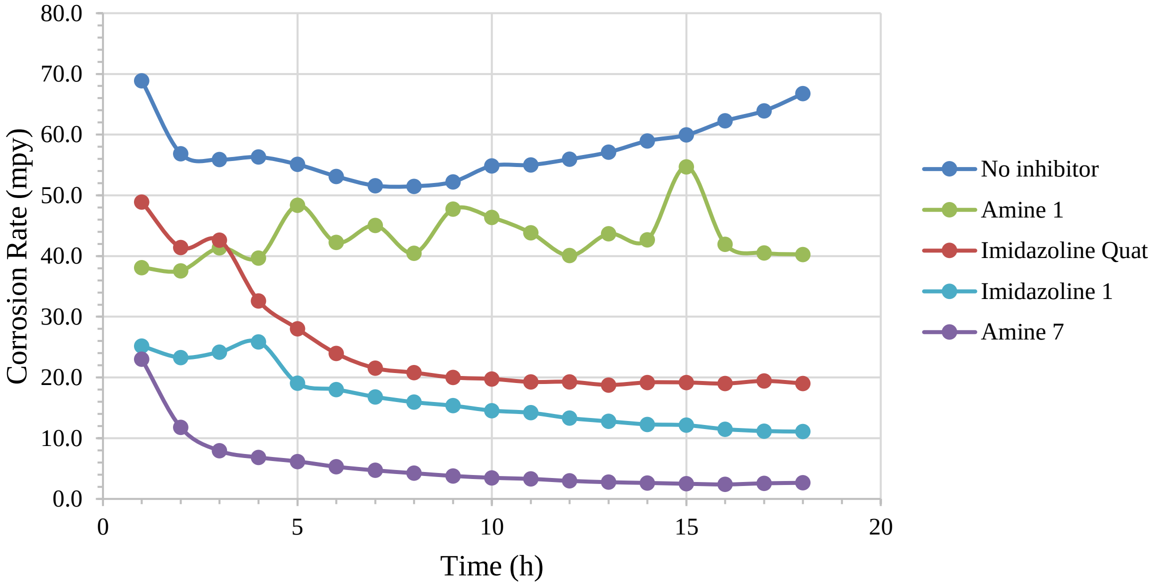


Figure 2. Corrosion rate of C1018 steel cylinders: 250 ppm of inhibitor, 400 rpm, 18 h, pH 7.4, air, 50 °C.

respectively. In both cases, the coupons ended with black deposits. It's possible that the reduced corrosion rates relative to the blank were due to the formation of a protective film from the corrosion products.

3.3 Electrochemical Evaluation of Inhibitors

Some of the leading candidates were then evaluated using electrochemistry. For the initial tests, a C1018 steel cylinder electrode was rotated at pH 7.4 for 18 hours. Air was bubbled through the solution for the duration of the test. These tests further narrowed down of the list of potential candidates. Several of the amine-based corrosion inhibitors provided good protection under these conditions. Amine 7 lowered the corrosion rate over the first 3 hours, such that it was below 10 mpy for hours 3-18. This amine was the best overall inhibitor under these conditions. Imidazoline 1 and imidazoline quat also provided good protection. Both inhibitors took several hours to establish some protection and ended with corrosion rates between 10-20 mpy at hour 18. Interestingly, amine 1 did not provide good protection. The corrosion rate was between 40 and 50 mpy for most of the experiment. Despite the high corrosion rate the coupon looked good visually and remained a light grey color. Presumably, amine 1 sequesters and removes oxidized iron from the surface, thereby cleaning the surface. This amine does not appear to form a protective film.

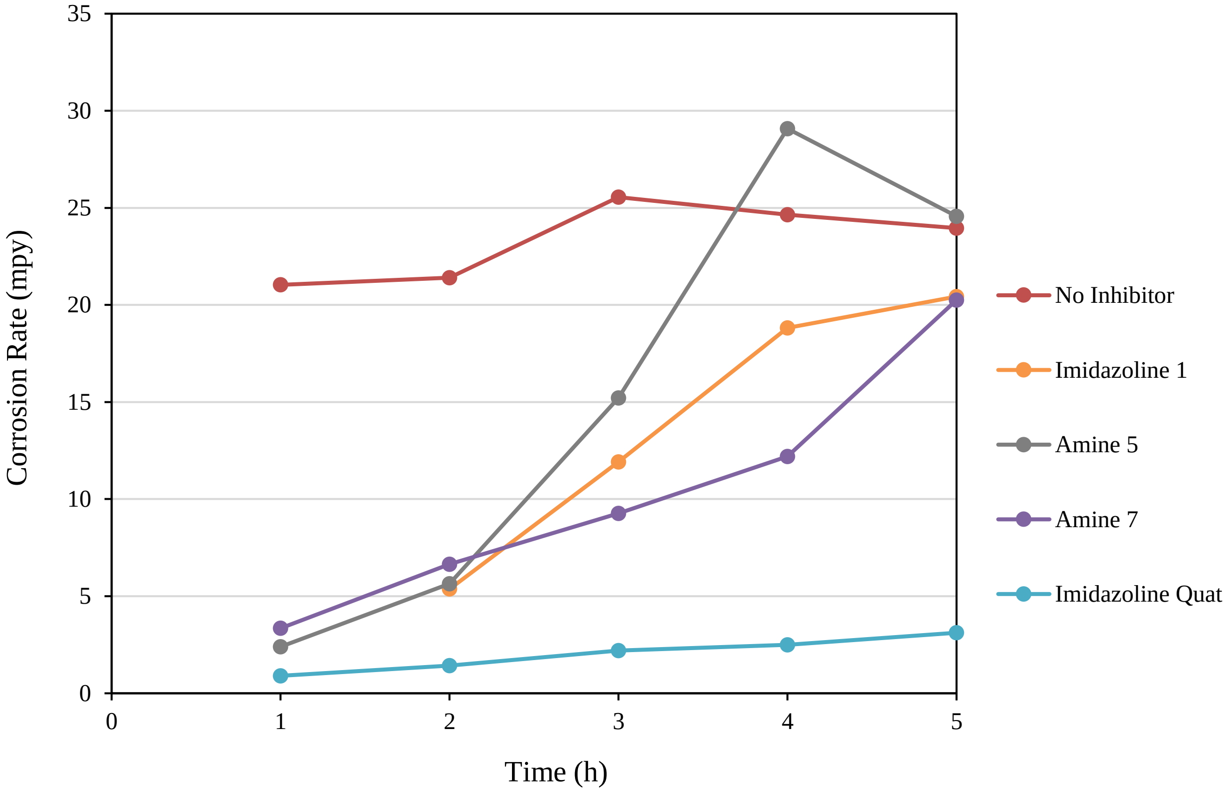
Although the results in air provided some interesting results, it was decided to run some additional experiments under conditions which were closer to geothermal conditions. First, a solution of geothermal brine described in Table 5 was preheated with 125 ppm of inhibitor to 70 °C and sparged the solution with CO_2. After 1 hour, a C1018 steel cylinder was submerged and rotated at 400 rpm. CO_2 was sparged throughout the experiment. Linear Polarization Resistance (LPR) experiments were run every hour for 5 hours, followed by Electrochemical Impedance Spectroscopy (EIS) after the fifth LPR run.

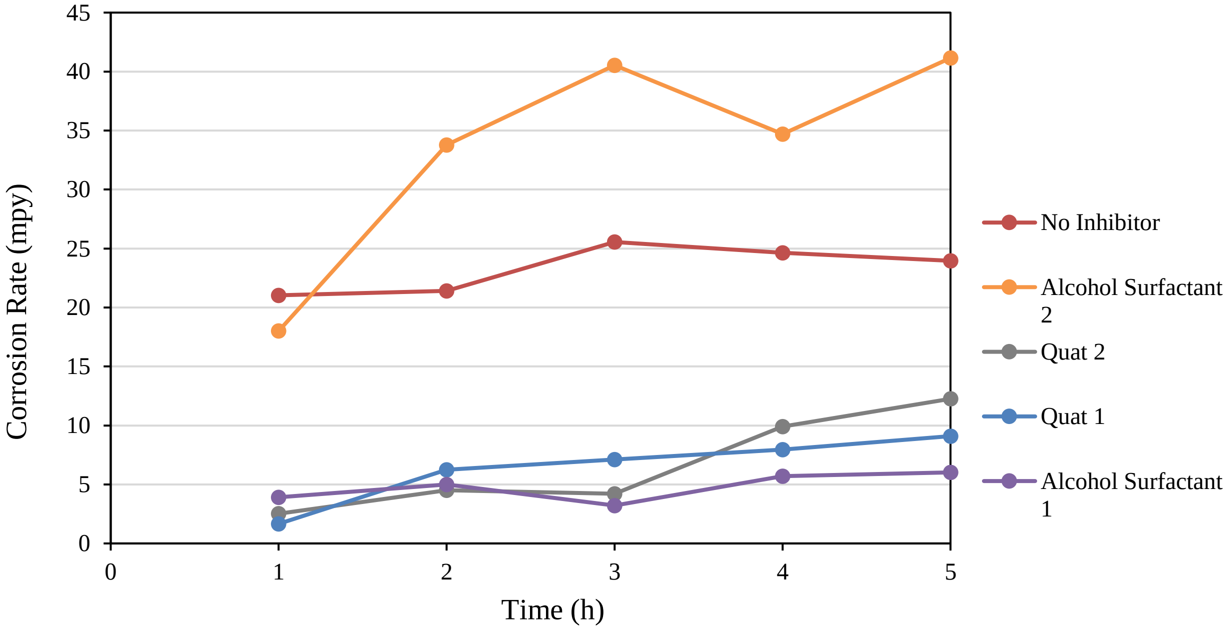
Table 5. Geothermal brine used for tests at pH 5.

Ion	Concentration
Cl^-	2000 ppm
SO_4^{2-}	40 ppm
Ca^{2+}	7 ppm
S^{2-}	25 ppm
pH	5.0

The results of the LPR experiments are presented in Figures 3a and 3b. Most of the amines provided good protection initially, but gradually lost protection over time as seen in Figure 3a. Amine 5, Amine 7 and Imidazoline 1 all had initial corrosion rates around or below 5 mpy. Overtime, Amine 7 and Imidazoline 1 gradually lost their efficacy and had a final corrosion rates of 20.3 mpy and 20.4 mpy, respectively. The untreated coupon ended with a corrosion rate of 24.0 mpy. Most of the efficacy of these inhibitors was lost over this 5 hour period. Amine 5 had even worse performance. The coupon treated with Amine 5 provided very good protection after 1 hour of exposed, 2.4 mpy, but after 5 hours of exposure had a corrosion rate of 24.6 mpy, which was worse than the untreated coupon.

In contrast, the Imidazoline Quat provided good protection throughout the 5 hour test. The corrosion rate began at 0.90 mpy after 1 hour and ended at 3.1 mpy after 5 hours of exposure. This represents an 87% reduction in the corrosion rate at hour 5. It appears that compounds with amine functional groups lose their efficacy over time. In contrast, compounds which do not have free amine groups, such as the





Top: Figure 3a. Corrosion rate of C1018 steel cylinders treated with 125 ppm of amine-based inhibitors, rotated at 400 rpm over 5 h at pH 5.0 with a CO_2 sparge at 70 ºC.

Bottom: Figure 3b. Corrosion rate of C1018 steel cylinders treated with 125 ppm of non-amine-based inhibitors, rotated at 400 rpm over 5 h at pH 5.0 with a CO_2 sparge at 70 ºC.

Imidazoline Quat, which has a quaternary ammonium group, do not lose a lot of efficacy over time. It's possible that the amine groups react with carbon dioxide, thereby losing efficacy over time. Amines are known to react with CO_2 to form carbamates and/or ammonium carbonates and are commonly used in carbon capture and storage.(Leung et al., 2014) It's possible that these reactions reduce the efficacy of these inhibitors leading to increased corrosion rates over time.

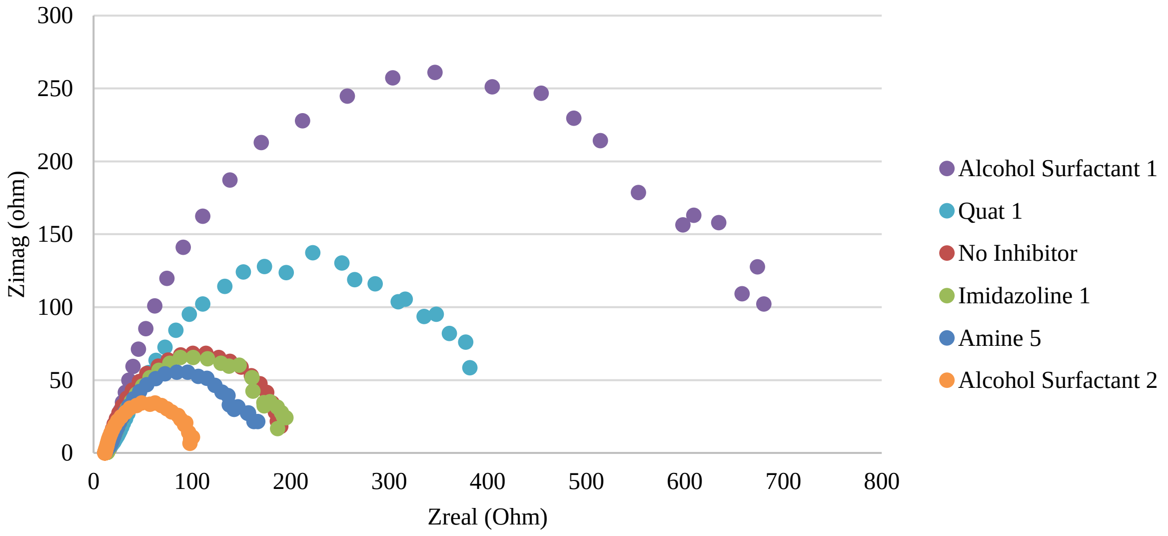


Figure 4. EIS plot of a C1018 cylinder treated with 125 ppm inhibitor after 5 hours in geothermal brine saturated with CO_2 at 70 ºC.

This theory was tested with other non-amine inhibitors. Both Quats 1 and 2 had low initial corrosion rates of 1.66 mpy and 2.52 mpy, respectively, after 1 hour of exposure. After 5 hours, coupons treated with Quats 1 and 2 had corrosion rates of 9.1 mpy and 12.3 mpy, respectively. These represent a reduction in corrosion rate of 62% and 49%, respectively. Alcohol Surfactant 1 was also very effective with a corrosion rate of 3.9 mpy after hour 1 and a corrosion rate of 6.0 mpy after 5 hours. This represents a 75% reduction in corrosion rate after 5 hours.

Unexpectedly, Alcohol Surfactant 2 did not provide good protection from corrosion. The corrosion rate after 1 hour was 18.0 mpy and ended at 41.1 mpy after 5 hours. This was significantly worse than the corrosion rate of the untreated coupons. After the run the coupon had visible signs of corrosion and had a dark grey appearance. This contrasts with the coupons treated with Alcohol Surfactant 1, which was light grey and did not have visible signs of corrosion.

After the fifth hour, the robustness of the film was measured using electrochemical impedance spectroscopy, as shown in Figure 4. The coupon treated with Imidazoline 1 had similar impedance to the coupon without any added inhibitor. This was expected since those coupons had a similar corrosion rates at hour 5 as measured by LPR. Amine 5, which had a slightly higher corrosion rate than the untreated coupon, also had a slightly lower impedance. Alcohol Surfactant 2 had a much lower impedance than all other corrosion inhibitors. It is possible that this surfactant reduces the surface tension of the water without forming any sort of protective layer. This leads to lower impedance and higher corrosion rates.

The data from Figure 4 was used to calculate the solution resistance R_s and the polarization resistance, R_p summarized in Table 6. As expected the solution resistance did not change significantly. The polarization resistance did vary substantially between the inhibitors. The compounds with the largest R_p were Quat 1 and Alcohol Surfactant 1. The R_p for quat 1 was 378 Ω, while the R_p for Alcohol Surfactant 1 was 690 Ω. This indicates that these inhibitors formed a robust protective layer, consistent with the low measured corrosion rate. Conversely, Amine 5 had a R_p of 152 Ω, while Alcohol Surfactant 2 had a R_p of 87 Ω. Both of these resistances were below the resistance of the untreated coupon which had a resistance of 179 Ω. These results confirm that there is an inverse correlation between the impedance and the corrosion rate. Higher impedance leads to higher polarization resistance, R_p, which leads to lower corrosion rates.

Table 6. Summary of resistances calculated from EIS curves in Figure 4.

Inhibitor	R_s (Ω)	R_s+R_p (Ω)	R_p (Ω)
No inhibitor	14	193	179
Alcohol Surfactant 1	12	702	690
Quat 1	12	390	378
Imidazoline 1	14	197	183
Amine 5	12	164	152
Alcohol Surfactant 2	11	98	87

4. CONCLUSION

Corrosion inhibitors were evaluated at neutral pH in air and acidic pH under a CO_2 atmosphere. It was determined that while amine-based inhibitors performed well at pH 7.4 they slowly lost efficacy at pH 5 in the presence of CO_2. It is possible that the CO_2 reacts with the inhibitors and reduces their effectiveness. Other inhibitors, such as quaternary ammonium compounds, imidazoline quats and alcohol surfactants all had much better efficacy in the presence of CO_2. These compounds all had robust films after 5 hours, as measured by EIS.

Future work will include testing at lower pH, 3.0, to determine the efficacy under more acidic conditions. The authors will continue to conduct lab tests under simulated geothermal conditions. We are looking for industry collaboration to further the work requiring specific well chemistries and side stream trials.

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