New highly thermally stable corrosion inhibitor for geothermal applications

Parravicini Davide[1], Guidetti Alessandro[1], Johnson Kuy[1]

[1] Italmatch Chemicals

d.parravicini@italmatch.com

Keywords: *corrosion, CO_2, geothermal, high temperature, inhibitor*

ABSTRACT

Corrosion can often happen in geothermal plants due to high temperature and the presence of significant number of chlorides in the liquid phase and CO_2 and H_2S in the gas phase. In some cases, the use of acid to reduce pH to delay amorphous silica formation, can increase the risk of corrosion issues that could eventually lead to loss of power or heat generation or, in severe cases, shutdowns to replace the corroded part of the plant. The use of corrosion resistant alloys is a currently used approach, but it increases CAPEX associated with a new geothermal plant. For this reason, effective treatment based on a corrosion inhibitor is becoming attractive. Due to the high temperature, most of the film forming corrosion inhibitor cannot be used as they rapidly degrade. In this work, to identify the most suitable solution, high temperature weight loss coupon test has been performed on several different technologies and the most promising was then evaluated under different conditions. Another important aspect is the interaction between scale and corrosion inhibitors that in some cases could lead to unexpected loss of performance in the field. A proper selection of these chemicals is crucial for obtaining the desired protection in the plant. This aspect was also evaluated in this paper, with both scaling and corrosion tests carried out in the presence of corrosion and scale inhibitors. After this extensive lab work, a field trial to confirm corrosion properties under real field conditions was scheduled. Details and results are discussed and analyzed in the paper.

1. INTRODUCTION

Geothermal energy is an attractive alternative to standard energy sources due to its environmental profile. However, corrosion and scale control in geothermal power production is a major hurdle in advancing the use of this renewable source of energy. High temperature represents an important challenge for most of the film forming corrosion inhibitors currently available as they easily degrade and/or create a film on metal surface which does not resist at high temperatures (Schott et al).

Corrosivity of geothermal brines is also increased by the presence of a significant amount of chlorides, high total dissolved solids (TDS), and dissolved gases such as H_2S and CO_2. Furthermore, pH modification processes to achieve pH 4.5-5.0 with mineral acids are used to prevent silica scale formation on the surface equipment and injection wells, but this pH reduction typically increases the corrosivity of the brine.

The aim of this work was to develop a new corrosion inhibitor able to provide good protection at high temperatures, working under conditions as close as possible to a real geothermal field.

2. EXPERIMENTAL

Weight Loss Coupon tests were performed at 80°C and 170°C to evaluate inhibition properties. Testing protocols are described in the sections below.

The brine used for the tests is a synthetic geothermal brine with high TDS and content of chlorides (Table 1). NaCl (ACS reagent, Sigma Aldrich), CaCl2*2H_2O (ACS reagent, Sigma Aldrich), $MgCl_2$*6H_2O (ACS reagent, Sigma Aldrich), KCl (ACS reagent, Sigma Aldrich), $SrCl_2$*6H_2O (ACS reagent, Sigma Aldrich), $BaCl_2$*2H_2O (ACS reagent, Sigma Aldrich), $NaHCO_3$*2H_2O (ACS reagent, Sigma Aldrich) and Na_2SO_4*10H_2O (ACS reagent, Sigma Aldrich) were used for the preparation of the brine. The testing brine is freshly prepared before every test.

10ppm of a proprietary scale inhibitor was added to the testing brine to avoid scale formation during the test. Any formation of scale on the metal coupons could lead to localized corrosion beneath it that cannot be prevented by the corrosion inhibitors.

Metal coupons used to evaluate corrosion rate were made of C1018 carbon steel. Corrosion rate was calculated with the following equation (NACE TM0169/G31):

$$Corrosion\ rate = (K \times W)/(A \times T \times D)$$

where:

K = constant

T = time of exposure in hours

A = area in cm^2

W = mass loss in grams

D = density in g/cm^3

ISSN 2703-4275

Geothermal brine (ppm)	
Na^+	27957
K^+	3893
Mg^{2+}	111
Ca^{2+}	7450
Sr^{2+}	492
Ba^{2+}	19.3
Cl^-	65027
SO_4^{2-}	76
HCO_3^-	173
SiO_2	170
pH	5.0-5.5

Table 1: Composition of the synthetic geothermal brine

2.1 Corrosion Inhibition Test at 80°C

A corrosion inhibition test at low temperature was performed using 1L glass bottles equipped with a PTFE holder for the metal coupons and a Binder M series oven to store testing bottles.

One liter of the brine is delivered into the glass bottles, then the required amount of additive is added (based on previous experience with this test and conditions, 50ppm were added). It should be noted that this dose rate is much higher compared to what is expected in this field as lab conditions are more severe for inhibitors. After the additions the solution is purged with nitrogen for 30 minutes to completely remove the oxygen and reach anoxic conditions. During the nitrogen purge metal coupons are installed on the PTFE holder. After 30 minutes the coupons are submerged in the brine and then the bottles are immediately sealed and placed in the oven at 80°C. After twenty-four hours the bottles are taken out of the oven. Metal coupons are polished with diluted HCl and weighed using an analytical scale. The bottle without the additive is labelled as blank.

2.2 Corrosion Inhibition Test at 170°C

Corrosion inhibition test at high temperature was performed using a Berghof BR-300 autoclave, capable of reaching a maximum temperature of 300°C and a 200 bar pressure. The inner vessel of the autoclave is made of PTFE to avoid any contamination during the tests.

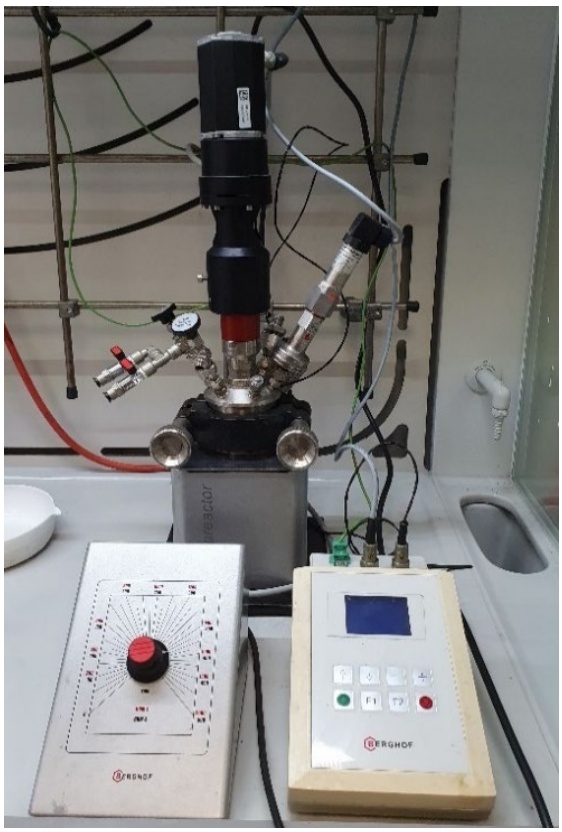

Figure 1. Berghof BR-300 autoclave

Testing protocol for the test at high temperature is similar to the protocol followed for the tests at 80°C. 200ml of the brine is delivered into the PTFE vessel, then the required amount of additive is added (also in this case 50ppm). After the additions the vessel is placed inside the autoclave and the solution is purged with nitrogen for 30 minutes to completely remove the oxygen. As for the previous test, coupons are installed on the PTFE holder. After 30 minutes of purging the coupons are completely submerged in the testing brine, the autoclave is sealed and heating is started. After six hours at 170°C the heater is turned off and the solution is left standing until it cools. The untreated solution is labelled as blank.

2.3 Barite static test

A static test was performed using a Binder M series oven to store the testing bottles and an Agilent 5800 ICP-OES to measure the residual barium in solution.

Due to the very low scaling tendency of the geothermal brine, the barite static test was performed with an internal standard brine with higher barium and sulphate content. Anionic and cationic brines were stored in the oven at 90°C before the test. 50ml of anionic brine is delivered into a 125ml glass bottle, then the additives are pipetted in the required amounts and in the end 50ml of cationic brine is quickly added. After the latter addition the bottles are immediately sealed and placed in the oven for ten minutes at 90°C, trying to simulate the residence time of the brine in the geothermal plant. After ten minutes a small aliquot from the solutions is taken to be analyzed by ICP-OES.

3. RESULTS

3.1 Blank test

A high temperature test in the autoclave was used as a screening test for many different technologies, including well-known and common film-forming corrosion inhibitors such as TOFA-DETA imidazoline and oleyl amine. For each product, a corrosion test was repeated at least twice to check reproducibility of results.

Corrosion Inhibitor technology	Avg. (mpy)
Blank	30.435
Benchmark 1	29.64
TOFA-DETA imidazoline	32.165
Oleylamine	34.025
Experimental 1	23.79
Experimental 2	22.595
Experimental 3	27.78
Experimental 4	18.21
Experimental 5	26.85
Experimental 6	24.19
Experimental 7	24.60
Experimental 8	25.93
Experimental 9	26.85
Experimental 10	31.37
Experimental 11	29.78

Table 2: High temperature weight loss coupon test

As expected, the high temperature and long residence time led to challenging conditions, and most of the technologies evaluated in this test (including TOFA-DETA imidazoline and oleylamine) provided low to negligible improvement in corrosion rate compared to blank. Most likely the poor results are related to the low thermal stability of the corrosion inhibitor chemistry and/or of the film formed on the metal surface.

However, Experimental 4 showed a significant decrease in the corrosion rate (40% less compared to blank), and appeared to be the most promising solution. Good results of Experimental 4 can also be visually observed in evaluating the metal coupon after the test (Figure 2).



Figure 2: Metal coupons after the high temperature corrosion test. Benchmark (right) and Experimental 4 (left)

The weight loss coupon test was then repeated at a low temperature (80°C) but with the testing time increased up to 24h. These conditions represent a standard for many applications. For this test, only the Benchmark and Experimental 4 were considered.

The low temperature leads to a lower corrosion rate for the blank, but also in this case, Experimental 4 provided a significant improvement outperforming the benchmark (Table 3).

Corrosion Inhibitor technology	Avg. (mpy)
Blank	8.64
Benchmark 1	12.56

ISSN 2703-4275

Experimental 4	4.92

Table 3: Low temperature weight loss coupon test

Figure 3 shows the testing bottles at the end of the test, confirming what was measured based on the weight of the coupons. Both Blank and Benchmark solutions were turbid with a significant amount of deposit (corrosion by-products) at the bottom while Experimental 4 bottle was clearer and the amount of deposit much smaller.

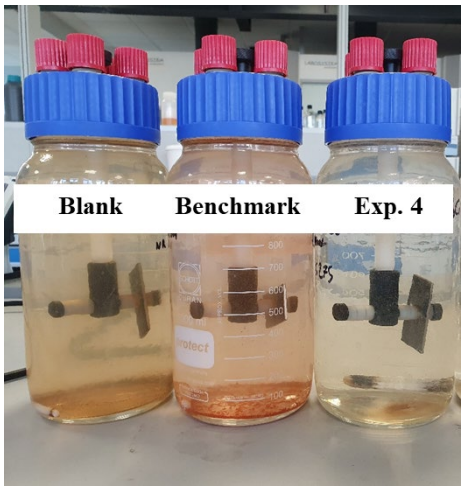

Figure 3: Weight Loss Coupon test at 80°C

Another important aspect to be considered during the development of corrosion inhibitors is their impact on scale inhibitor performance as they are often dosed together in the same pipeline and in some cases there could be a negative impact on the performance of both chemicals (Scheiber et al).

A simple static test was performed, comparing performance of the scale inhibitor without and with Experimental 4 corrosion inhibitor against Barite.

The testing time and SI / CI ratio were selected to mimic a real field application.

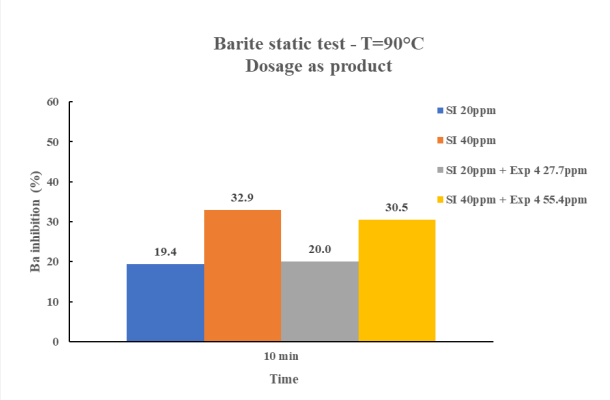

Figure 4: Barite static test – effect of corrosion inhibitor on scale inhibitor performance

Tests results confirmed that Experimental 4 has no impact on the performance of the scale inhibitor, as the inhibition efficiency remained constant with and without the corrosion inhibitor.

After the thermal aging Geogard SB2, no significant changes in the product appearance were observed and, when the performance test was repeated, no loss in performance was observed (Fig. 3), with Geogard SB2 showing the same combination of inhibition and dispersion properties were observed as with the unaged sample.

4. FIELD TRIAL

To confirm the promising results obtained in the lab, a 3-months field trial has been scheduled in a geothermal plant in Europe. Corrosion coupons will be located in the plant pipeline and the technical performance of the product will be evaluated after three weeks. Other KPIs are brine composition and heat-exchanger or plant pressure.

At the time of writing this paper, the field trial was ongoing and only partial results about plant pressure and brine composition were available, without highlighting any significant change after dosing started.Although these results are not enough from which to draw conclusion, they provide an indication that this new corrosion inhibitor is compatible with the brine and does not create clogging in the pipeline.

5. CONCLUSION

The tests performed in the lab provided promising results in terms of corrosion inhibition and good indication about the best performing chemical blend when comparing a number of different and well-known chemistries. Despite all the efforts on testing the different chemistries at lab scale, it is very difficult to be able to properly simulate the real field condition of a given geothermal plant and it is not practically feasible to simulate all the existing geothermal plant due to high variability in terms of operating conditions (temperature, pressure, fluid velocity, gas/liquid ratio and chemical composition). It is therefore recommended to run onsite trials to monitor the performance of the chemistry blend selected at a lab scale. We have been working with geothermal operators to plan for field trials in the coming months.

ACKNOWLEDGEMENTS

The authors would like to thank the Technical Committee and Italmatch Chemicals and its Center of Expertise.

REFERENCES

Schott T., Liautaud F., December 2022, “Monitoring and Mitigating Corrosion in Geothermal Systems”, Material and Corrosion, Volume 73, Issue 12, Pages 1916-1942

NACE International, October 2012, "Standard Guide for Laboratory Immersion Corrosion Testing of Metals", NACE TM0169/G31

Scheiber, J.; Seibt, A.; Jähnichen, S.; Degering, D.; Mouchot, J. 11-14 June 2019, Combined Application of Inhibitors for Scale and Corrosion Mitigation: Lessons Learned. Proceedings, European Geothermal Congress, Den Haag, The Netherlands