EVALUATION OF PERFORMANCE PROBLEMS OF CALCITE INHIBITORS. FINDINGS AND SOLUTIONS.

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ABSTRACT

This is a research project aimed at improving the efficiency, effectiveness and cost of calcite inhibition for the geothermal industry. It is aimed at providing updated data and support to the developing geothermal industry technologies of recent years including binary and Enhanced Geothermal System (EGS). It is common knowledge that many inhibitors used in Geothermal are borrowed from a range of other industries that include the paint industry, paper, boiler, cooling water and mining. Variable results and reports from industry users have flagged the need for some geothermal specific R&D into calcite inhibition.

In the last eight years there have been advancements in calcite inhibition and modelling. Whilst presented to the geothermal industry as improvements there are common mismatches between modelled dose rates and rates that geothermal sites actually need to use and in instances, some catastrophic performance failures causing plant shut downs. It became apparent that little work had been done outside of the basic NACE test screening to understand what geothermal specific conditions can impact calcite inhibition performance in the geothermal world.

Phase one of the research project screened 14 inhibitors using standard NACE testing without deaeration at 250 °C and 300 °C. The tests were then repeated with small amounts of cations added to the synthetic brines used in the NACE test that are commonly found in geothermal brines. These included: Fe, Mn, As, Sb, and Al. Results varied from product to product but demonstrated that some experienced a 90% drop in performance explaining the results in the field. These results are reported in this paper.

Phase two of the project is to qualify what inhibitors work best in the presence of some of the cations tested in order to enable more accurate modelling and prediction of what would be best suited to any particular brine chemistry.

Phase three of the project is to find or develop additives that mitigate the negative impacts of the interfering substances.

1. INTRODUCTION

WATCH24 (Stefán et al., 1982) is an industry standard for modelling geothermal brines. This program is used widely for predicting the saturation indices of many species. Other software, like PHREEQC, have also been used to model geothermal systems (Na, 2010). However these tools stop there. Tools that are used to indicate preferred solutions and dose rates are proprietary and focus usually on the host company's products, dosage guidelines (Gill and Rodman, 2015, Gill, 2017) and internal methods of determining dose rates. Using lab synthetic brines in conjunction with the standard NACE test do not take the brine characteristics of the specific geothermal plant into consideration and therefore can give very different performance results than what would be experienced in the field.

Reports from companies that final dose rates are often very different to the calculated, or sold rates, have prompted this investigation into quantifying some of the impacts that some common constituents found in geothermal brines can have on common calcite inhibitors. This investigation was initially a pilot to relate the NACE-based performance of products used in geothermal to actual performance using NACE methods, but spiked with commonly found cations in geothermal brines.

The results from the pilot trials confirmed anecdotal reports from the field that actual use rates can be up to five times the modelled prediction and, in some cases, the apparent complete failure of the calcite inhibitor.

These results prompted a Solenis R&D project specific to calcite inhibition in geothermal applications. The stages of this work include the first phase reported in this paper, a second phase qualifying what chemistries perform best against the different elements tested and a third phase to determine specific additives that can mitigate the impact of these elements often found in geothermal brines that decrease the inhibitor's performance.

2. CALCIUM CARBONATE SCALE FORMATION

Geothermal brines are often at or near saturation with respect to calcite under reservoir conditions (Jacobo et al., 2012, Lee et al., 2015, Siega et al., 2005). Flashing of the brine in the wellbore or above ground in a steam separator transfers carbon dioxide and other non-condensable gases to the steam phase. This release of carbon dioxide raises the pH of the brine and subsequently increases carbonate ion concentration (Arnorsson, 1989). When the decrease in carbon dioxide partial pressure is sufficient to lead to supersaturation, calcite precipitation occurs:

$Ca^{+2} + 2HCO_3^- \leftrightarrow CaCO_3\,(s) + CO_2\,(g) + H_2O$

If calcite deposition begins to occur in a wellbore, it is often in a relatively small zone where steam begins to form. Once precipitation begins, flow within the well may quickly become restricted as exhibited in Figure 1. Reduction in well output results in a decline in power output by the geothermal plant.

Numerous chemistries have been employed with varying success to mitigate calcium carbonate deposition in geothermal brines. Organic phosphonates were traditionally utilised (Corsi, 1986, Parlaktuna et al., 1989), but are typically limited to lower temperature wells due to the potential for thermal degradation to orthophosphate, which hinders performance and may lead to calcium phosphate deposition. Polyacrylic acid products are commonly employed, but are reported to be limited in temperature range with thermal degradation and loss of performance in wells above 250 °C (Siega et al., 2005). Product impurities, such as sulphur, can lead to deposit formation within the capillary injection tubing (Moya et al., 2005). Additionally, overdosing of polyacylates can lead to a tenacious calcium acrylate deposit, especially at lower pH values in binary plants (Muller and Rodman, 2014). More recently, the successful use of polyamino polyether methylene phosphonate (PAPEMP) for calcite scale control has been described in multiple geothermal applications (Gill, 2011, Jacobo et al., 2012, Mejorada et al., 2011, Pereira, 2014).

Figure 1. Calcium carbonate scale formation due to geothermal brine.

3. EXPERIMENTAL

Calcium carbonate inhibition testing was conducted following the NACE Standard protocol (NACE International) with the synthetic brine chemistry listed in Table 1, except the test flasks were not saturated with carbon dioxide. Prior to inhibition testing, 10 weight % antiscalant solutions were autoclaved at 250 or 300 °C to mimic downhole geothermal conditions. Results from further testing under deoxygenated conditions will be conducted and compared with those reported here. Calcium carbonate scale inhibition was calculated with the following equation:

$$\% \text{ Inhibition} = (C_a - C_b) / (C_c - C_b) \times 100$$

Where:

C_a = Ca^{2+} concentration in the treated sample after precipitation

C_b = Ca^{2+} concentration in the blank after precipitation

C_c = Ca^{2+} concentration in the blank before precipitation

The tests were then repeated with small amounts of cations added to the synthetic brines used in the NACE test that are commonly found in geothermal brines. These included: Fe, Mn (found sometimes in shallow bores), As, Sb, and Al. The inhibition rates obtained in the non-spiked samples were compared and results graphed. The impacts of the spiked brines on the different calcite inhibitors are discussed in the section below.

Table 1. Synthetic brine chemistry used in testing.

Ion	Concentration (ppm)
Ca^{+2} as $CaCO_3$	4100
Mg^{+2} as $CaCO_3$	900
Na^+	14,000
HCO_3^-	2700
Cl^-	23,600

4. RESULTS AND DISCUSSION

4.1. Initial Product Screening

Laboratory calcium inhibition results for nine products (samples P1 to P9) are reported in Figure 2: a commercial polyacrylate homopolymer (P1), carboxylate copolymer antiscalant products (P2 – P8) and a blend of a carboxylate homopolymer and a carboxylate copolymer (P9). The single active inhibitors (P1 – P8) were dosed at approximately 65 ppm as product, whereas the blended inhibitor (P9) was dosed at 30 ppm as product. In this study, all products were tested under three thermal conditions: without any thermal treatment, after autoclaving for 3.5 hours at 250 °C or after autoclaving for one hour at 300 °C.

For all of the tested products, significant (at least 16%) decrease in inhibition performance was measured after autoclaving at 300 °C for one hour. At the lower temperature of 250 °C, four products, P1, P2, P4 and P5, exhibited essentially no loss of performance. However, the other products in this study lost significant inhibition efficacy (14 – 34%) even under these milder conditions. These test results indicate that a decline in inhibitor performance is likely in geothermal wells that approach or exceed 300 °C and selection of antiscalant chemistry is critical to mitigate performance loss in lower temperature wells. Additional testing showed that time and temperature both determine the amount of decline. Based on this further testing is planned to dive deeper into the impact of temperature alone.

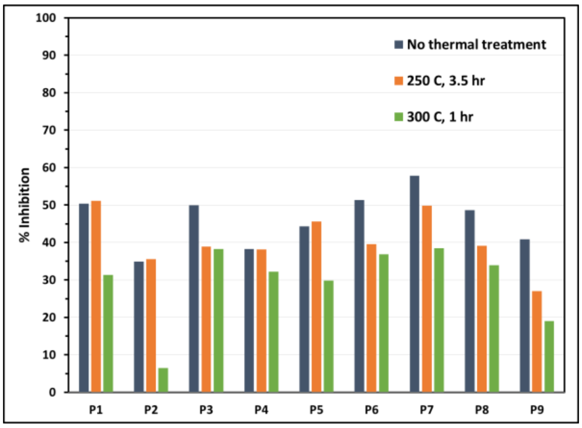


Figure 2. Calcium inhibition results for selected antiscalant products without thermal treatment, autoclaved at 250 °C for 3.5 hours and autoclaved at 300 °C for one hour.

Additionally, two additional commercial polyacrylate homopolymers (P10 and P11) were evaluated at lower product dosages (2 – 20 ppm as product). Select antiscalant products, including P4 and P7 from the previous screening, and additional carboxylate copolymers (P11 and P12) were also tested at lower dosages. The calcium inhibition results for this study, where the antiscalants were autoclaved for one hour at 250 °C, are presented in Figure 3.

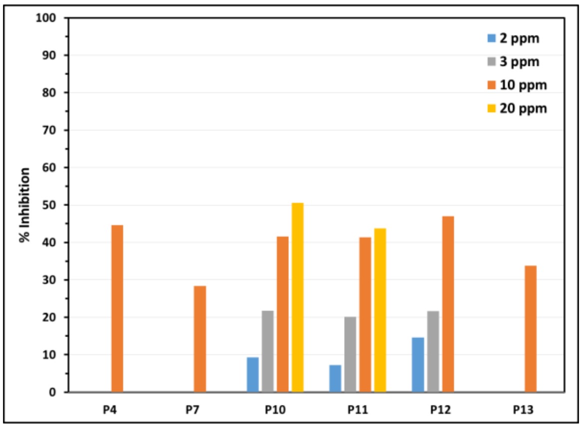


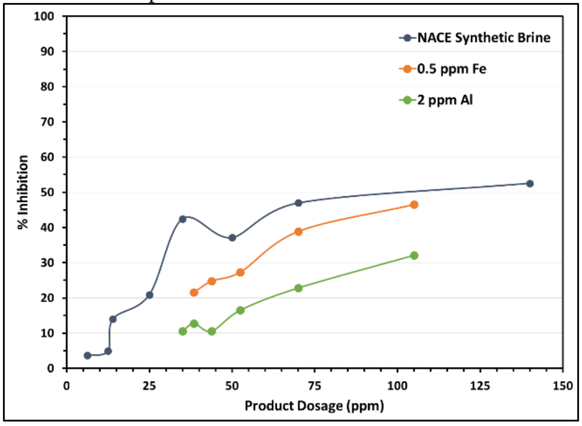
Figure 3. Calcium inhibition results for inhibitors at varying dosages after autoclaving at 250 °C for one hour.

Increasing the dosage of P10, P11 and P12 from 2 to 10 ppm significantly improved their measured calcium carbonate inhibition values from less than 15% to greater than 40%. However, doubling the dosages of P10 or P11 from 10 to 20 ppm yielded much smaller incremental improvements, suggesting a plateau in performance for these products in this test methodology.

These results reflect the different mechanisms by which the two commercial polyacrylate homopolymers (P10 and P11) and additional carboxylate copolymer (P12) work, where slight under dosing can result in a nonlinear decrease in calcite inhibition. These lab results indicate a potential for catastrophic failure in the field if the inhibitor is under dosed.

4.2. Impact of Contaminants on Calcium Inhibition

Two common metal cations found in geothermal brines, iron and aluminum, were spiked into the NACE standard brine. The impact of 0.5 ppm iron and 2 ppm of aluminum on antiscalant product P9 are summarized in Figure **4**. Under these testing conditions, aluminum had a much larger impact on calcium carbonate inhibition as compared to iron, albeit at a higher concentration of contaminant.



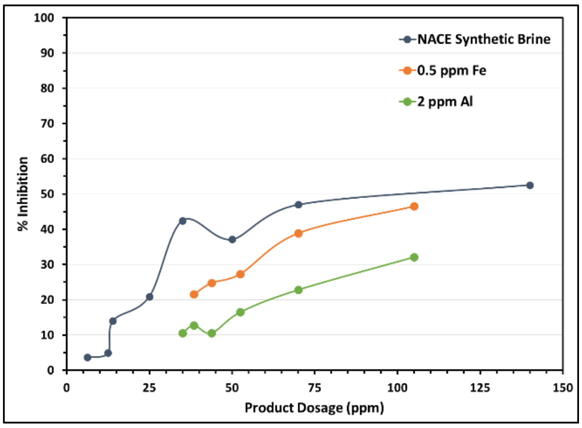


Figure 4. Calcium inhibition of varying dosages of P9 in the presence of iron or aluminum after autoclaving at 250 °C for one hour.

Additional testing was conducted using the NACE synthetic brine with added aluminum concentrations of 0.5 and 1 ppm. As displayed in Figure 5, the calcium carbonate inhibition efficiency of P4, P10, P11, P12, P14 (a blend of a carboxylate homopolymer and a carboxylate copolymer similar to P9) and P15 (a blend of P4 and P10) were impacted by aluminum “poisoning” to vary degrees. The polyacrylic acid homopolymers, P10 and P11, were relatively robust in the presence of 1 ppm of Al with inhibition declines of less than 25%. The P12 carboxylate homopolymer was acutely impacted with an inhibition efficacy drop of 31%. In the 0.5 ppm of Al tests, P10 and P15 yielded the smallest declines in performance (less than 5%).

4.3 Synthesis of results

4.3.1 Impact of cations Fe and Al

It is apparent that the presence of aluminum impacts the performance of all of the tested inhibitors to differing degrees. When this is combined with the data from thermal treatment, these compounding effects can be significant. Further complicating matters are the data that indicate that performance by some of the copolymer and polyacrylate products is via threshold inhibition, whereby insufficient dosage can cause significant impacts in the field. Some of the polymers used for calcite inhibition are significantly impacted by aluminum (e.g., the P12 carboxylate copolymer). However, this highlights the need for additional research to explore the efficacy of this polymer with another antiscalant product as a means of mitigating the impact of aluminum. These results will be used in stage three of the investigation.

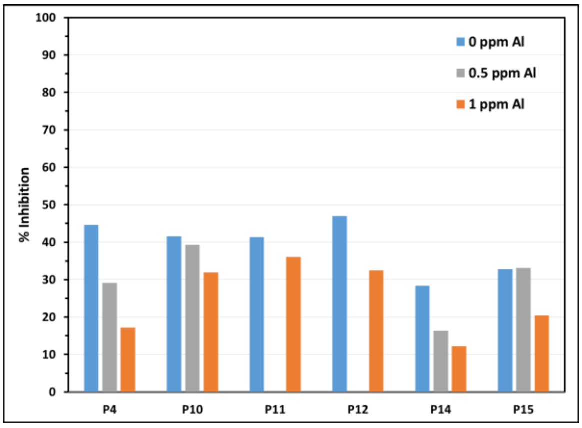


Figure 5. Impact of varying concentrations of aluminum on calcium inhibition for antiscalant products. All inhibitors were autoclaved at 250 °C for one hour prior to testing. Note that P11 and P12 were not tested in the presence of 0.5 ppm Al.

4.3.2 Heating time

All the inhibitors are affected as they undergo heating. Understanding the matrix of time and temperature is an area that the authors believe could benefit from more study. It suffices to say that a product that works well at 180 °C, but significantly degrades at 300 °C, should not be discredited if the temperature at which it will used is 180 °C. An example of this is the comparative field work done by Muller and Rodman comparing the effectiveness of a copolymer and a polymaleic acid (PMA) (Muller and Rodman, 2014). The PMA blend actually removed deposits even though they are not considered thermally stable at higher temperatures (Amjad and Zuhl, 2005).

The final temperature any particular inhibitor will reach is dictated by the characteristics of the geothermal reservoir. However, the time an antiscalant is exposed to elevated temperatures can be influenced by altering pumping rates. It is not uncommon to see pumps rated at 20 litres per hour used for downhole dosing, which has the effect of having to use higher concentrations of the inhibitor that get exposed to the higher temperatures for longer. A 6 mm dosing tube has a volume of about 28 litres (Ramos-Candelaria et al., 2000, Moya et al., 2005), therefore at 20 litres per hour the inhibitor is "cooked" for 1 hour 24 minutes. If the same inhibitor were to be dosed at 50 litres per hour (with the proportional dilution), it would only be "cooked" for 33 minutes.

Geothermal companies that experience issues with blockages in their dosing tubing often see a gum-like deposit on the end of the weight and sometime flakes of shellac type deposits. As can been seen from Figure 6, these blockages may be due to degradation of the inhibitor when exposed to elevated temperatures.

Figure 6. Sample of a 10% solution of P9 after autoclaving at 250 °C for one hour.

5. SUMMARY

It is clearly apparent that more work is needed to advance calcite inhibition effectiveness and efficiency for the geothermal industry.

Thermal degradation could be further defined and quantified, as some products in this study lost significant inhibition efficacy (14 – 34%) under the milder conditions of 250 °C "cooking". However, there are several sites in New Zealand and globally that are less than 200 °C and many secondary use applications that are far lower. These test results indicate that a decline in inhibitor performance is likely in geothermal wells that approach or exceed 300 °C and selection of antiscalant chemistry is critical to mitigate performance loss. However, in lower temperature wells/applications the use of less thermally stable products may provide more cost effective inhibition. Thus, the impact of temperature profiles and preheating have been included in further studies. Testing showed that time and temperature both determine the amount of decline.

Another reason for the differences between calculated dose rates and rates that are actually required in the field to inhibit calcite have been investigated. It is apparent that the presence of cations such as iron and aluminum have notable impacts on many inhibitors. If the actual brine water profile is not taken into consideration in the process used by proprietary "dose rate" calculators, then it seems very likely that there could be significant differences between what is calculated and what is required in the field. Particularly, if iron and/or aluminum are present.

This study also showed that the relationship between dosage rate and inhibition is not linear. The combined effects of temperature, interference of inhibition effectiveness by cations and pumping rates are all possible reasons why the product and dosage rate provided by a chemical company has appeared to not work at all in the field.

Further stages of investigation will include gaining a deeper understanding of the effects of temperature and time on a range of chemical inhibitors, the comparative performance of different inhibition chemistries in the presence of commonly occurring 'poisons' in geothermal brines and the enhancement of calcite inhibition in the presence of these poisoning species.

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