Investigation of the Effects of Metal Cations on Polycarboxylate Calcite Inhibitors

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ABSTRACT
Geochemical modelling tools developed to generate calcite inhibitor dosage recommendations have been observed to exhibit a mismatch between the predicted antiscalant dosages and the actual, necessary inhibitor concentration. In some cases, these discrepancies have led to rapid calcite scale formation, catastrophic performance failures and plant shutdowns due to underdosing of the inhibitor. Performance issues like these highlight the necessity for additional research to develop next generation antiscalant chemistries and more accurate product dosage models. This paper describes laboratory testing of a series of carboxylic acid-based polymeric calcite inhibitors after thermal exposure at 200 °C using a NACE testing protocol. Variables examined included the effect of varying carboxylate functionality and molecular weight on performance in the presence of several known, potentially interfering, metal cation species. These new insights into the differences in performance of these calcium carbonate inhibitor chemistries will result in improved product selection and more accurate product dosing models for geothermal applications.

1. Introduction

1.1 Calcium Carbonate Scale Formation and Mitigation
A major operational issue for many geothermal plants is calcium carbonate deposition in production wellbores or above ground at the steam separator. This precipitation process occurs when geothermal brines, which are at or near saturation with respect to calcite (the most stable and common polymorph of calcium carbonate), flash, thereby releasing carbon dioxide and other non-condensable gases into the steam phase. This transfer of carbon dioxide raises the pH of the remaining brine and subsequently causes a shift in the bicarbonate/carbonate equilibrium toward increasing carbonate ion concentration (Arnórsson, 1989). Flashing also concentrates the
remaining ions, including calcium, in the brine. When the decrease in carbon dioxide partial pressure is sufficient to lead to supersaturation, calcite precipitation occurs according to Equation 1:

\[ \text{Ca}^{2+} + 2\text{HCO}_3^- \leftrightarrow \text{CaCO}_3 (s) + \text{CO}_2 (g) + \text{H}_2\text{O} \]  

(1)

When calcite precipitation occurs within a production wellbore, deposition typically occurs within a narrow vertical zone near the flash point. The rate of scale growth is dictated primarily by the calcite supersaturation index (CSI); however, other factors, such as fluid dynamics with the wellbore, also are thought to have an impact (Quinao et al., 2017). Eventually, the calcite blockage (see Figure 1) can restrict flow of brine within the production well causing a decline in power output of the geothermal plant. Recovery of full production can be obtained via mechanical or chemical cleaning of the production wellbore. However, these options are expensive, with costs that may exceed $1 million, and must be accomplished while the well is offline (Siega et al. 2018). Acidizing with strong acids also increases the potential for corrosion of the wellbore casing.

Alternatively, calcium carbonate scaling within production wellbores has been successfully managed with the addition of inhibitor chemistries. The antiscalant is added via a capillary to a zone below the flash point to ensure adequate mixing within the brine. Installation costs for an inhibitor dosing system and the annual chemical expenditure vary because they depend on the specifics of the brine flow rate and the dosage necessary for effective scale control. However, because using chemical antiscalants for calcite mitigation decreases downtime, increases production rates and extends time between well cleanings, their use has been an economically viable long-term solution for many geothermal well operators.

![Figure 1: Example of calcium carbonate deposition in a geothermal process.](image)
A wide range of antiscalant chemistries has been used with differing degrees of success to prevent calcite deposition in geothermal well applications. While organic phosphonates have proven highly effective under laboratory conditions, significant thermal degradation was noted at 210 °C, which doubles the necessary concentration for comparable inhibition performance (Corsi, 1986) and greatly limits their applicability to low temperature production wells. Decomposition of phosphonates to orthophosphate also generates the potential for calcium phosphate precipitation and scale formation. Similar to calcium carbonate, tricalcium phosphate and hydroxyapatite (two crystalline forms of calcium phosphate) have retrograde solubility and are highly sensitive to pH (Stumm and Morgan, 1996). More recently, polyamino polyether methylene phosphonate (PAPEMP) has been reported to be an effective calcite scale inhibitor in geothermal fields in Papua New Guinea (Mejorada et al., 2011), El Salvador (Jacobo et al., 2012) and the Azores (Pereira 2014). Laboratory testing conducted at 250 °C in a synthetic brine suggested that PAPEMP is hydrothermally stable under these conditions; however, only limited long-term field data under high temperature conditions appears to exist for this chemistry at this time.

Over the past two decades, carboxylic acid-based polymeric antiscalants have become the most commonly used products for calcite inhibition. However, these chemistries also have had performance challenges. A previous report highlighted that product impurities such as sulfur can lead to corrosion and deposition of corrosion byproducts in the capillary injection tubing (Moya et al., 2005). Furthermore, a poly(acrylic acid) inhibitor was found to be susceptible to thermal degradation and loss of performance when used in wells at temperatures greater than 250 °C (Siega et al., 2005). The same report concluded that while poly(maleic acid) was more tolerant to thermal stressing, thermal degradation still occurred when the product was exposed to a high temperature brine (~255–260 °C) for an extended period of time (Gill, 2011). Lastly, it was noted that overdosing of a poly(acrylic acid) antiscalant can result in tenacious calcium polyacrylate deposits as the result of acidic brine conditions encountered in binary plants (Muller and Rodman, 2014).

1.2 Modelling of Scale Formation in Geothermal Applications

Estimation of the propensity for mineral scale formation can be accomplished by calculating the activity coefficient product, \( Q \), and the solubility product, \( K \), for a given geothermal brine chemistry and application temperature. The saturation index (\( SI \)) is then defined in Equation 2 as:

\[
SI = \log \left( \frac{Q}{K} \right)
\]

where at equilibrium, \( Q \) and \( K \) are equal and the \( SI \) is 0. Calculation of \( SI \) values greater or less than 0 are indicative of supersaturation and undersaturation, respectively. Estimation of \( SI \) values for geothermal applications has been greatly aided by advancements in modelling software. Since its development nearly 40 years ago, WATCH (Arnórsson et al., 1982) has become the industry standard for aquatic speciation calculations to model geothermal brines. Other geochemical software, such as PHREEQC (Na, 2010) and SOLVEQ (Bartolo, 2015), also have been used for simulations of geothermal processes. Generally, these programs are used to estimate the aqueous speciation of geothermal brines in production wells based on analytical values from steam and water samples collected at the surface as the input. With the aid of
modelling software, $SI$ values over a wide range of temperatures and operational scenarios can be calculated quickly to provide estimates of the potential for formation of calcium carbonate and other inorganic scaling species.

More recent improvements in geothermal modelling tools have included software programs to provide a recommended antiscalant product and dosage based on $SI$ calculations and operational conditions (Gill and Rodman, 2015; Gill, 2017). Although these tools represent an advancement in the geothermal industry, they are limited, typically, to a small set of inhibitor products, and the underlying dosing guidelines are proprietary. Furthermore, geothermal field operators have reported that the actual antiscalant dosage necessary to prevent calcite formation can be very different than the dosage calculated by the modelling tool. In some cases, these discrepancies have led to underdosing of calcite inhibitors, thereby causing severe scale blockages and a general distrust of the inhibitor dosing models.

2. Experimental Methods

Laboratory calcium carbonate inhibition testing followed the NACE standard protocol (NACE International, 2001) using the synthetic brine summarized in Table 1, except the test solutions were not saturated with carbon dioxide prior to heating. The NACE standard test methodology commonly has been employed in the geothermal industry to screen inhibitor chemistries under simulated downhole conditions (Siega et al., 2018). Prior to inhibition testing, 10 weight % antiscalant solutions were purged with nitrogen for 30 minutes to deaerate the samples and then were thermally treated in an autoclave. The temperature profile, which consisted of a 45-minute temperature ramp from the ambient temperature to 200 °C, a 60-minute hold period and then a 45-minute cool down to ambient conditions, was controlled via a proportional integral derivative (PID) controller, electric resistive heating and a water-cooled cooling loop. This ensured a consistent thermal history for each antiscalant.

| Table 1. Synthetic brine chemistry used in NACE calcium carbonate inhibition 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         |

The inhibitors used in this testing were comprised of a series of polymers derived from two different carboxylic acid monomers of varying composition and molecular weight (summarized in Table 2). According to the coding in Table 2, samples designated “Polym-01” through “Polym-05” are homopolymers of Monomer 1 of varying molecular weight; samples designated “Polym-06” through “Polym-09” are copolymers of various ratios of Monomer 1 and Monomer 2 with a molecular weight comparable to “Polym-05”; and the sample designated “Polym-10” is a homopolymer of Monomer 2 with a molecular weight comparable to “Polym-05”.

Thermally treated inhibitor samples were added to the synthetic brine at varying dosages and incubated at 70 °C for 18 hours. After incubation, the samples were filtered through a #5 Whatman filter to remove any precipitant and were analyzed for calcium content by titration.
Each experiment was conducted in triplicate. Calcium carbonate scale inhibition was calculated using Equation 3:

\[
\% \text{ Inhibition} = \frac{(C_a - C_b)}{(C_c - C_b)} \times 100
\]  

(3)

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

### Table 2. Summary of characteristics of the polymers used in laboratory testing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Monomer 1</th>
<th>Monomer 2</th>
<th>Relative Mw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polym-01</td>
<td>++ + + +</td>
<td>-</td>
<td>+ + + +</td>
</tr>
<tr>
<td>Polym-02</td>
<td>+ + + +</td>
<td>-</td>
<td>+ + +</td>
</tr>
<tr>
<td>Polym-03</td>
<td>+ + + +</td>
<td>-</td>
<td>+ +</td>
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<tr>
<td>Polym-04</td>
<td>+ + + +</td>
<td>-</td>
<td>+ +</td>
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<tr>
<td>Polym-05</td>
<td>+ + + +</td>
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<td>+</td>
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<td>Polym-06</td>
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<td>Polym-07</td>
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<td>Polym-08</td>
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<td>+</td>
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<tr>
<td>Polym-09</td>
<td>+</td>
<td>+ + + +</td>
<td>+</td>
</tr>
<tr>
<td>Polym-10</td>
<td>-</td>
<td>+ + + +</td>
<td>+</td>
</tr>
</tbody>
</table>

Calcite inhibition tests also were conducted using low levels of metal cations added to the standard synthetic brine in Table 1. Stock solutions of reagent grade salts of aluminum chloride, iron(II) sulfate heptahydrate and manganese(II) chloride tetrahydrate were prepared and dosed to the test samples to achieve the desired concentrations of soluble aluminum, iron and manganese. The impact of these cation “poisons” at varying levels as compared to the results without the contaminants are summarized in the following section.

### 3. Experimental Results

#### 3.1 Calcium Carbonate Inhibition

Calcium threshold inhibition results at three different dosages are reported in Figure 2. All products were tested on an equal solids basis because of differences in actives concentrations between the polymer samples.

For the Monomer 1 homopolymer series (Polym-01 through Polym-05), increasing calcium carbonate inhibition was observed at the threshold 1.5 ppm dosage level with greater than a five-fold improvement between Polym-01 and Polym-05. This advancement in performance is in accordance with the decreasing trend in molecular weights of these polymers. These results also are in agreement with the general observation that lower molecular weight polymers (greater than a minimum value) yield superior threshold inhibition functionality, whereas higher molecular polymers provide improved dispersion properties (Standish, 2015).
Increasing the antiscalant dosages from 1.5 to 5 ppm greatly enhanced the performance of all of the Monomer 1 homopolymers; however, doubling their dosages to 10 ppm resulted in minimal improvements in effectiveness. Furthermore, the differences in product performance for the Monomer 1 homopolymers were much less significant at the highest tested dosage (~15% deviation between the best and worst performers at 10 ppm). These results suggest that an ultimate limit on performance exists for this chemistry under these test conditions. While variances in molecular weight of the Monomer 1 homopolymers generated measurable differences in calcium carbonate inhibition efficacy, other factors, such as molecular weight distribution, initiator chemistries and chain transfer agent, also may play a role in the overall effectiveness of these polymers.

![Bar chart](image)

**Figure 2: Laboratory calcium carbonate inhibition results for samples at multiple dosages after purging with nitrogen and autoclaving at 200 °C.**

Samples Polym-06 through Polym-10 were screened to examine whether incorporation of various levels of another carboxylic acid monomer into the polymer matrix (Monomer 2) provided any additional improvement in performance. Based on the results from the Monomer 1 homopolymer series, low molecular weight candidates were targeted. Overall, the Monomer 2-containing polymers yielded poorer calcium carbonate inhibition performance as compared to the Monomer 1 homopolymer inhibitors. Increasing the Monomer 2 content of the polymers generally had an increasingly negative effect on calcite inhibition efficacy.

### 3.2 Impact of Aluminum on Calcium Carbonate Inhibition

Previous laboratory work (Muller et al., 2018) indicated that as little as 0.5 ppm of soluble aluminum could have severe, deleterious effects on the performance of calcium carbonate inhibitors. However, certain product chemistries also were determined to be much less
susceptible, even when “poisoned” with 1 ppm of aluminum. The aim of this testing was to expand upon these initial findings to explore the impact of polymer composition and molecular weight on inhibition properties in the presence of aluminum.

Results of calcium carbonate inhibition testing using the NACE synthetic brine with an added aluminum concentration of 1 ppm are summarized in Figure 3. An inhibitor dosage of 5 ppm (as solids) was chosen to maximize differentiation of product performance. While the presence of aluminum acutely reduced the performance of Polym-01 and Polym-04 by 15% or more, Polym-02, Polym-03 and Polym-05 exhibited much more robust behavior. Since molecular weight does not appear to be the primary factor that dictates aluminum tolerance of the Monomer 1 homopolymers, other, more subtle, characteristics related to their manufacture must be considered. Future laboratory synthesis and testing is planned to explore these parameters in more depth to provide a better understanding of structure-property relationships and to develop improved, aluminum-tolerant inhibitors.

![Figure 3: Impact of 1 ppm of aluminum on calcium carbonate inhibition for samples at a test concentration of 5 ppm (as solids).](image)

All of the Monomer 2 containing polymers were influenced by the addition of 1 ppm of aluminum resulting in a decrease of inhibition performance of 7% (Polym-08) to 21% (Polym-06). No clear correlation in carboxylic acid monomer content and tolerance toward aluminum is evident in these results. However, when combined with the Monomer 1 homopolymer series results, these findings confirm that certain inhibitor chemistries are less sensitive to aluminum poisoning.
3.3 Impact of Iron on Calcium Carbonate Inhibition

Selected samples also were tested in the presence of 1 and 3 ppm of soluble iron. These values were chosen because naturally occurring iron concentrations of greater than 2 ppm have been measured in production wells in the Cerro Prieto geothermal field of Mexico (Armienta et al., 2014). The impact of iron on the calcite inhibition performance of these antiscalants is summarized in Figure 4. Like the aluminum poisoning tests, the inhibitor dosage was kept constant at 5 ppm (as solids) to try to maximize differentiation in product performance.

The addition of 1 ppm of soluble iron proved acutely deleterious to the calcite inhibition of all of the tested antiscalants. The minimum decline in product efficacy was approximately 30% for Polym-03 and Polym-05, whereas the two tested Monomer 2-containing polymers, Polym-07 and Polym-09, proved especially intolerant to 1 ppm of iron (the decrease in inhibition was approximately 90% for both products). At 3 ppm of soluble iron, complete loss of performance was observed for all of the tested calcite inhibitors (i.e., no difference existed between the treated and untreated samples). Additional, limited testing (not shown here) indicated that product dosages of 10 ppm (as solids) with 1 ppm of iron yielded comparable results to a dosage of 5 ppm (as solids). These preliminary results suggest that much higher inhibitor concentrations may be required in geothermal brines that contain significant levels of iron, and additional development of iron-tolerant antiscalants is necessary.
### 3.4 Impact of Manganese on Calcium Carbonate Inhibition

Like iron, manganese has been observed at elevated concentrations (greater than 4 ppm) in the Cerro Prieto geothermal field (Bliss, 1995). As previously described with the aluminum and iron poisoning tests, the inhibitor dosage was held constant at 5 ppm (as solids). Initial testing with up to 10 ppm of soluble manganese revealed a measurable decline in calcite inhibition performance for only one of the three tested Monomer 1 homopolymer antiscalants (Polym-01, see Figure 5). The other two products, Polym-02 and Polym-05, did not exhibit any loss in performance, despite the excessive concentration of soluble manganese. More work with additional inhibitor chemistries is planned to explore further the interactions between molecular weight, functionality and tolerance toward this toxic metal.

![Figure 5: Impact of varying concentrations of soluble manganese on calcium carbonate inhibition for selected samples at a test concentration of 5 ppm (as solids).](image)

### 4. Discussion

The standard NACE protocol with thermal stability testing has proven to be a useful screening tool to investigate the efficacy of carboxylic acid-based polymers for calcium carbonate scale inhibition. Furthermore, these initial results have yielded insights into physical (e.g., molecular weight) and chemical parameters that can be tuned within these synthetic polymer systems to optimize inhibition performance. The Monomer 1 homopolymer antiscalants proved superior to the Monomer 2-containing polymers with increasing concentrations of Monomer 2 resulting in poorer performance. Among the Monomer 1 homopolymer inhibitors, decreasing the polymer molecular weight had a positive effect on threshold inhibition performance. Additional laboratory testing using an alternative test methodology, such as capillary tube blocking, would be required to evaluate the dispersion properties of these products.
Dosing low levels of metal cations to the standard synthetic NACE brine has generated an additional factor to consider when screening potential antiscalant chemistries. While previous studies revealed the acute impact soluble iron and aluminum can have on inhibitor chemistries, these reports were limited to calcium phosphate antiscalants under simulated cooling water conditions (Zuhl et al., 1987; Amjad et al., 2001). Additionally, the effect of soluble manganese on polymeric scale inhibitors does not seem to be well studied in geothermal or cooling water applications. While multiple Monomer 1 homopolymer products proved to have robust calcite inhibition performance in the presence of 1 ppm of aluminum, none of the tested products were immune to the poisoning effect of 1 ppm iron. Identification of iron-tolerant antiscalants remains an unmet need.

5. Conclusions

Further systematic research is needed to discover improved calcite antiscalants and to characterize the causes of differences in modelled and actual inhibitor dosages. This work identified that varying the molecular weight of the Monomer 1 homopolymer antiscalants and modifying the molar ratio of monomers in the Monomer 2-containing copolymers could have a significant effect on product performance in standard NACE testing. Additionally, the impact that aluminum, iron and manganese have on these scale control chemistries was quantified. For geothermal brines that contain significant levels of these impurities (1 ppm or even less for iron and aluminum), calculating the calcite saturation index alone is insufficient to yield an accurate estimation of antiscalant dosage. This simplification of dosing guidelines is likely one of the causes of inhibitor underdosing and the resulting loss of trust in calcite antiscalant modelling tools.

Future phases of this research project will include exploring the impact of elevated temperatures (250–300 °C) on calcite inhibitors and additional quantification of the impact of common impurities in geothermal brines. Synthesis work is also planned to produce additional modified antiscalants with the objective of developing higher performing, more poison tolerant calcite inhibitors.

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