

Evaluation of Calcite Scale Inhibitors: Impact of Metal Cations

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ABSTRACT

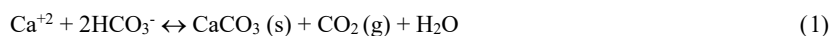
Over the past decade, electrolyte modeling software has been combined with proprietary scale inhibitor dosing guidelines to generate product dosages based on site-specific brine chemistries and operating conditions. While these programs signify a great advancement to geothermal plant operators, there is often a significant discrepancy in the recommended dosage and the necessary inhibitor concentration needed for effective scale control. In some cases, underdosing of a calcite antiscalant has led to severe scale formation and unanticipated plant shutdowns. Failures like these have emphasized the need for additional research to develop improved scale inhibitor dosing guidelines and more robust antiscalant chemistries. This paper summarizes laboratory performance testing of polymeric inhibitors after thermal treatment using a NACE calcium carbonate test protocol. The presence of metal cations commonly found in geothermal brines, such as aluminum and iron, was determined to have varying deleterious effects on antiscalant performance. The impact of the metal cations was dependent on concentration and scale inhibitor chemistry. Quantification of these negative effects on calcite inhibition performance will lead to the development of increasingly accurate and robust product dosage models for geothermal applications.

1. INTRODUCTION

Calcium carbonate scaling is experienced in nearly every geothermal field in the world. In severe cases, calcite formation in the production wells and surface equipment causes significant reductions in brine flow rates (Durak et al., 1993; Allan et al., 2019). This, in turn, can directly lead to a decline in output of the geothermal power plant. While still a major operational challenge for geothermal plants, the impact of calcium carbonate deposition can be monitored and minimized with chemical or mechanical treatment strategies.

1.1 Calcium Carbonate Deposition

Geothermal reservoirs are generally at or near equilibrium with respect to calcite, which is the most stable and common polymorph of calcium carbonate (Arnórsson, 1989). As compressed liquid brine flows into and ascends a production wellbore, the pressure decreases until the saturation pressure of the liquid is reached and vapor begins to form. The depth at which this process occurs is called the flash point, boiling point or bubble point (Michels, 1992). At the bubble point, carbon dioxide transfers from the liquid to the newly formed vapor phase. This loss of CO₂ results in an increase in pH in the remaining brine and a subsequent shift in the bicarbonate/carbonate equilibrium toward increasing carbonate ion concentration. Simultaneously, boiling concentrates the ions, including calcium and carbonate, in the liquid phase. When the decrease in CO₂ is sufficient to lead to supersaturation, calcite precipitation occurs according to Equation 1:



If calcite deposition occurs within a production well, the scale thickness typically increases rapidly from the bubble point to a maximum before tapering off. Detailed scale thickness profiles have been characterized in wells in the Dixie Valley geothermal field (Benoit, 1987). This has led to the development of semi-empirical models to predict the location and extent of calcite deposition in operating production wells (Michels, 1992; Allan et al., 2019).

1.2 Modeling of Scale Formation in Geothermal Applications

Estimating the likelihood of scale formation in geothermal production wells or separation equipment can be accomplished by calculating the saturation index (SI) of a given mineral using brine chemistry data and application temperatures. The SI is determined from the activity coefficient product, Q , and solubility product, K , as shown in Equation 2:

$$SI = \log\left(\frac{Q}{K}\right) \quad (2)$$

At equilibrium (the saturation point), Q and K are equal, the SI value is 0 and further precipitation or dissolution will not occur. Conversely, SI values greater or less than 0 correspond to supersaturated and undersaturated conditions, respectively. Calculation of SI values in geothermal systems has been greatly assisted by the development of geochemical modeling software over the past 40 years. WATCH (Arnórsson et al., 1982; Arnórsson et al., 1983), which was designed specifically for geothermal systems, has been the most extensively used software in the geothermal industry. However, other geochemical programs, such as PHREEQC (Na, 2010; Akin et al., 2015) and SOLVEQ (Todaka et al., 1995; Bartolo, 2015), have also been successfully used for simulations of geothermal processes. Modeling the chemical speciation of geothermal brines in production wells requires the input of accurate analytical data from both water and steam samples that are collected at the surface after flashing. Once the appropriate analytical data are entered into the software, the SI values for mineral species in the model database can be quickly calculated over varying temperatures and

operational conditions. While the onset of calcite scale growth is primarily dictated by a brine's SI value, fluid dynamics (Quinao et al., 2017) and the degree of flashing (Todaka et al., 1995) also may play a role. Lastly, these geochemical models are purely thermodynamic models, which do not address the kinetics of mineral precipitation. Calcite can rapidly crystallize and lead to deposition, whereas quartz is not likely to deposit even after exceeding its saturation point due to very slow crystal formation kinetics.

1.3 Deposition Prevention and Removal

Once calcite deposition begins to occur in a production wellbore (Figure 1), the blockage can eventually become severe enough to restrict brine flow and cause a decline in power generation. By monitoring brine flow rates and wellhead pressures, geothermal plant operators can proactively remove deposits with mechanical or chemical cleaning to maintain peak plant efficiency. In some cases, mechanical cleaning of production wellbores can be done online while the well is still operating and can quickly (within one day) return a well to its original operating capacity (Allan et al., 2019). Alternatively, chemical cleaning with a strong acid (mixed with a corrosion inhibitor to protect the well casing) can clear scale deposits in the wellbore or reservoir feed zone. Mechanical and chemical cleaning come at a cost with expenses recently estimated at \$0.5 - \$2 million for major clean-out operations (Siega et al., 2018).



Figure 1: Examples of calcium carbonate deposition in a geothermal process. The image on the right is adapted from Haizlip et al., 2012.

The use of chemical inhibitors for the prevention of calcium carbonate deposition in geothermal fluids has been practiced, with varying success, for approximately 40 years. Downhole injection of antiscalants is typically accomplished via capillary tubing that can be lowered to a desired depth. Ideally, the inhibitor addition point is well below (100 m or more) the bubble point to ensure adequate mixing with the brine (Siega et al., 2018). While the costs associated with the antiscalant feed system are significant (\$300,000 or more depending on the complexity of the installation), chemical inhibitors are often a cost-effective solution for calcite deposition control. With an effective dosage of a high-performing antiscalant, geothermal plant operators can greatly extend the time between necessary production well cleanings, decrease downtime and increase power production.

Some of the pioneering laboratory research and field testing concerned with calcium carbonate inhibition in geothermal applications was conducted over 30 years ago by Vetter and Campbell (1979) in the United States and by Corsi and coworkers (1985) in Italy. These researchers identified organic phosphonates as highly effective calcite antiscalants, but also noted that these chemistries were susceptible to thermal degradation under geothermal conditions. After thermal treatment at 210 °C, the necessary inhibitor dosage for calcite carbonate scale prevention was doubled as compared to samples heat-treated at 175 °C (Corsi et al., 1985). More recent reports have described the successful use of an alternative organic phosphonate, polyamino polyether methylene phosphonate (PAPEMP), as a calcite inhibitor in geothermal fields in Papua New Guinea (Mejorada et al., 2011), El Salvador (Jacobo et al., 2012) and the Azores (Pereira, 2014). Additional laboratory testing conducted at 250 °C in a synthetic brine suggested that PAPEMP was hydrothermally stable under these conditions (Gill, 2011). However, only limited long-term field data under high temperature conditions appears to exist for this inhibitor at this time. In addition to higher chemical treatment costs, decomposition of organic phosphonates to orthophosphate can cause the deposition of calcium phosphate in high hardness brines. Like calcium carbonate, tricalcium phosphate and hydroxyapatite are sparingly soluble mineral salts with retrograde solubility and are highly sensitive to changes in pH (Stumm and Morgan, 1996).

In addition to organic phosphonates, carboxylic acid-based polymeric antiscalants have been tested for calcite inhibition. While these chemistries have become the most widely used products, there have also been reported performance issues. Product impurities can react with the injection tubing, which can lead to corrosion and deposition of corrosion byproducts in the dosing capillary (Moya et al., 2005). Like organic phosphonates, polycarboxylates may also be susceptible to thermal degradation under certain geothermal conditions. Siega and coworkers (2005) reported the loss of performance and the presence of black deposits due to decomposition when a poly(acrylic acid) inhibitor was dosed into a well at temperatures in excess of 250 °C. The same report concluded that a poly(maleic acid) product was more thermally robust, but thermal degradation was still noted when the antiscalant was exposed to a

temperature of ~255°-260 °C for an extended period of time. Finally, Muller and Rodman (2014) reported the presence of a tenacious calcium polyacrylate deposit as the result of overdosing a poly(acrylic acid) inhibitor in a binary plant.

These previous studies highlight the need for high purity inhibitors, careful selection of products for high enthalpy production wells and the risk of overdosing an antiscalant product. To aid in the selection and calculation of inhibitor dosages, algorithms have been developed that are based on calculated SI values and process conditions (Gill et al., 2015; Gill and Rodman, 2017). These tools are potentially a great value to the geothermal industry and plant operators. However, there have been reports of underdosing based on inaccurate dosing guidelines. When the actual necessary antiscalant dosage to prevent calcium carbonate deposition is significantly higher than recommended dosage, severe scaling can rapidly occur. This generates a distrust in the inhibitor dosing models and a potential loss of revenue for the geothermal power plant.

2. EXPERIMENTAL METHODS

Thermal stability testing was conducted with 10 weight % inhibitor solutions prepared in deionized water. After purging with nitrogen for 30 minutes to deaerate the samples, the products were heated in a 200-mL Parr (Moline, IL, USA) autoclave with a Pyrex¹ liner. The temperature profile of the solutions consisted of a 45-minute temperature ramp from ambient temperature to 200° or 250 °C, a 60-minute hold period and a 45-minute cool down to ambient conditions. This process was controlled via a proportional integral derivative (PID) controller, electric resistive heating and a water-cooled cooling loop to ensure that each inhibitor had a similar thermal history. Static calcium carbonate inhibition testing was conducted with the thermally treated antiscalants following the NACE standard protocol (NACE International, 2001), except that sample solutions were not saturated with carbon dioxide prior to heating. This methodology, which used the synthetic brine summarized in Table 1, has been used in previous geothermal studies to screen inhibitor chemistries under simulated downhole conditions (Robson and Stevens, 1989; Mejorada et al., 2011; Siega et al., 2018).

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

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:

$$\% \text{ Inhibition} = (C_a - C_b) / (C_c - C_b) \times 100 \quad (3)$$

where:

C_a = Ca²⁺ concentration in the treated sample after precipitation

C_b = Ca²⁺ concentration in the blank after precipitation

C_c = Ca²⁺ concentration in the blank before precipitation

The NACE calcite inhibition test methodology was also modified to include low levels of metal cations in the standard synthetic brine in Table 1. Stock solutions of reagent grade salts of aluminum chloride and iron (II) sulfate heptahydrate were prepared and dosed to the test samples to achieve the desired concentrations of soluble aluminum and iron. The effect of these “poisons” at varying levels as compared to the results without the contaminants are summarized in the following section.

Antiscalant products were also provided to GNS Science (Taupo, New Zealand) for thermal stability and NACE calcite inhibition testing. Inhibitor samples were diluted in deionized water (10% by volume) and placed in ½-inch diameter 316 stainless steel tubes capped with Swagelok (Solon, OH, USA) fittings under a nitrogen blanket. The tubes were then placed in a forced-draft oven at 300 °C ± 1 °C for four hours. Subsequent inhibition testing followed the NACE standard methodology, except 100 mL bottles were used with 80 mL solution rather than 125 mL bottles with 100 mL of test solution. Each experiment was conducted in duplicate.

The antiscalants used in this testing comprised of carboxylate-based polymers of varying composition and molecular weight. Inhibitors A, B and C were homopolymers, while samples D and E were copolymers. These chemistries have been utilized in geothermal processes and other high temperature applications for calcite scale inhibition. These polymeric products with and without thermal treatment were characterized via size exclusion chromatography (SEC) using a Waters (Milford, MA, USA) Alliance 2695 High Performance Liquid Chromatography system equipped with Suprema Linear S columns (PSS, Mainz, Germany) and a differential refractometer. Samples were run at 30 °C with a flow rate of 0.8 mL/min using a 0.1 M sodium nitrate/20% acetonitrile mixture as the mobile phase. Polydispersities were estimated with narrow molecular weight polymer standards.

¹ Pyrex[®] is a registered trademark of Corning Inc., Corning, NY, USA.

3. EXPERIMENTAL RESULTS

Calcium threshold inhibition results from NACE testing for five polymeric inhibitors at varying dosages are summarized in the following sections. Additionally, the effects of thermal treatment and metal cations on calcite inhibition performance are explored. Lastly, the impact of temperature on the molecular weight distributions of these antiscalant products is summarized.

3.1 Impact of Dosage and Temperature on Calcite Inhibition Performance

Calcium carbonate inhibition results for the five inhibitors in this study at three dosages (1.5, 5 and 10 ppm) are presented in Figure 2. Samples were thermally treated for one hour at 200° or 250 °C. In this testing, all products were tested on an equal solids basis due to differences in actives concentrations of the samples.

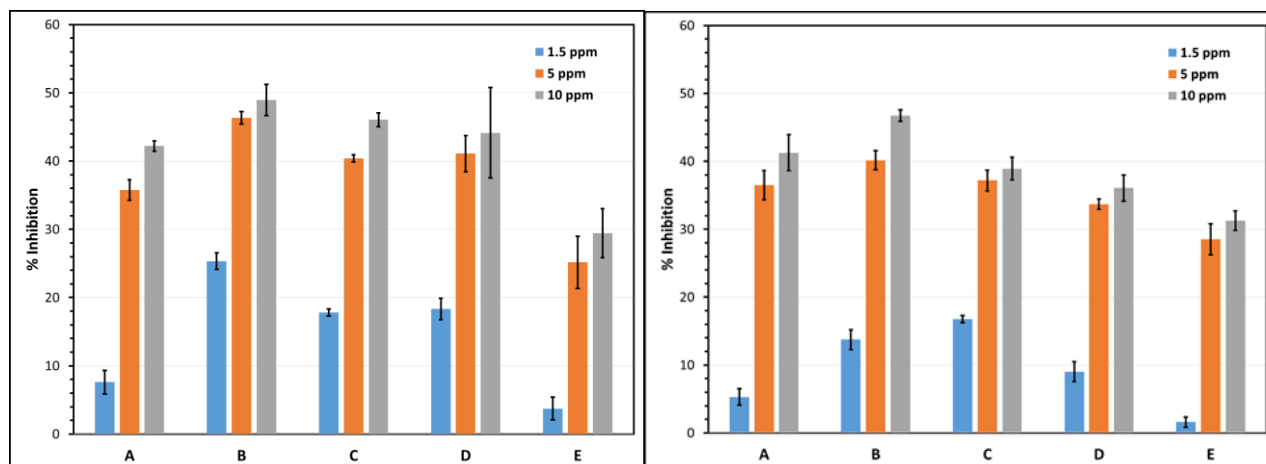


Figure 2: Laboratory calcium carbonate inhibition results for samples at multiple dosages after purging with nitrogen and autoclaving at 200 °C (left) and 250 °C (right).

After heat treatment at 200 °C, inhibitors B, C and D yielded superior performance when compared to inhibitors A and E at a dosage of 1.5 ppm. Increasing the antiscalant dosages from 1.5 to 5 ppm significantly increased the inhibition results for all the products, with inhibitor E resulting in nearly a six-fold improvement. However, inhibitors B, C and D remained the most effective (product A lagged just slightly behind). Doubling the dosages from 5 to 10 ppm resulted in minimal (6-18%) improvements in efficacy for all of the products, with some of the data within the statistical uncertainty of the experiments.

Similar dosage responses were observed with the inhibitor samples autoclaved at 250 °C. Like at 200 °C, products B, C and D produced the highest threshold inhibition performance at a dosage of 1.5 ppm. Increasing the product dosages to 5 ppm again resulted in greatly enhanced performance, whereas increasing the product concentrations to 10 ppm yielded a minor (5-16%) additional boost in efficacy. The dosage response results at 200 and 250 °C appear to signify an ultimate performance limit for these materials under these test conditions. This is also consistent with previous preliminary testing (Muller et al., 2018).

The largest impact of heat treatment was evident when comparing the calcium carbonate inhibition results when the samples were dosed at 1.5 ppm. All of the antiscalants yielded poorer results after autoclaving at 250 °C. However, the decline in performance for inhibitor C was only 6%, which was nearly comparable to the results from inhibitor B. At the higher dosages of 5 and 10 ppm, the impact of the higher autoclaving temperature was much less noticeable. Other than inhibitor D, which had a performance decline of 22%, all of the products displayed little loss of effectiveness (less than 20%) at 250 °C as compared to 200 °C. However, even these modest decreases in antiscalant efficacy could be significant, especially for high enthalpy geothermal production wells.

Laboratory calcite threshold inhibition data collected by GNS Science for the same five inhibitors with and without thermal treatment are displayed in Figure 3. All testing by GNS Science was conducted at an antiscalant dosage of 5 ppm as product.

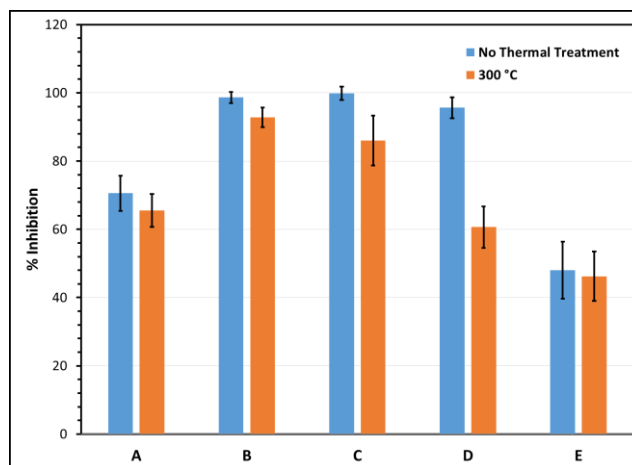


Figure 3: Calcium carbonate inhibition results collected by GNS Science. Thermally treated samples were heated at 300 °C for four hours prior to testing. All samples were tested at a concentration of 5 ppm (as product).

For the samples without thermal treatment, inhibitors B, C and D delivered the highest inhibition rates with nearly complete inhibition (96% or greater). Heating the antiscalant samples at 300 °C for four hours had varying effects on product performance. Inhibitors A, B and E were largely unaffected by the autoclaving with inhibition losses of only 4-7%, whereas inhibitors C and D suffered declines of 14% and 37%, respectively. Despite the loss of efficacy, inhibitor C still had the second highest inhibition performance at 300 °C, with only inhibitor B yielding a superior result.

While the GNS Science data in Figure 3 cannot be strictly compared to the results in Figure 2 due to differences in product dosages, autoclaving procedures, laboratory methods and laboratory personnel, trends in product performance can be identified. Inhibitors B and C consistently yielded the highest inhibition results, regardless of thermal history. Product D, which demonstrated similar efficacy compared to antiscalants B and C at lower temperatures (no heat treatment or 200 °C), decreased in effectiveness after autoclaving 250 °C and severely declined after thermal exposure at 300 °C. Inhibitors A and E, while demonstrating robust thermal stability in all of the laboratory testing, overall, did not perform as well.

3.2 Characterization of Inhibitor Samples after Thermal Treatment

In order to gain additional insights into the effect of thermal treatment on these inhibitor products, samples before and after autoclaving were characterized via SEC. SEC can quantitatively (relative to polymer standards) yield molecular weight distributions of polymeric materials and highlight changes in polymer chain architecture due to thermal degradation or other deleterious processes (Trathnigg, 2000).

Examples of SEC results for all five inhibitors are displayed in Figures 4-7. The three homopolymers in this study, A, B and C, were relatively monodisperse with minor peaks of varying magnitudes at longer elution times, which correspond to lower molecular weight materials. These data are consistent with previously reported results for low molecular weight, solution polymers used for scale control (Amjad et al., 2010). Inhibitors A and B exhibited essentially no change in molecular weight distribution after heat treatment at 200 or 250 °C. This is especially visible in the almost perfect overlay of the SEC traces in Figure 4 for antiscalant A. Furthermore, the weight-average molecular weights (M_w) for samples A and B are within 3%, regardless of thermal history. Inhibitor C exhibited no change in molecular weight distribution after autoclaving at 200 °C (Figure 6). However, after thermal treatment at 250 °C, there was a noticeable shift in peak position to a longer elution time, which corresponded to a 10% decrease in M_w .

The two copolymers, inhibitors D and E, were more polydisperse as compared to the homopolymers in this study (Figure 7). The SEC traces for inhibitor D consisted of a single, broad peak, whereas product E yielded a bimodal distribution of two populations of polymeric materials of varying molecular weights. Additionally, after autoclaving at 250 °C, the calculated M_w values for these two antiscalants decreased by ~35%. This transformation is apparent in the shift rightward to longer elution times, which is indicative of the generation of lower molecular weight materials.

Visual differences in some of the antiscalant samples were also apparent after thermal treatment, as exhibited for select products in Figure 8. No noticeable modification in appearance (presence of haziness, discoloring, precipitation, etc.) was visible for inhibitor A after autoclaving at 250 °C, which was consistent with the lack of change in the molecular weight distribution of this sample (Figure 4). Conversely, heat treatment of inhibitor E at 250 °C caused severe yellowing and formation of a white precipitant. This visual evidence in combination with the SEC molecular characterization data (Figure 7) seems consistent with previous reports of chain scission and the degradation of functional groups in carboxylate-based homo- and co-polymers after heat treatment (Lépine and Gilbert, 2002; Amjad, 2006). However, further analytical testing would be required to confirm this hypothesis.

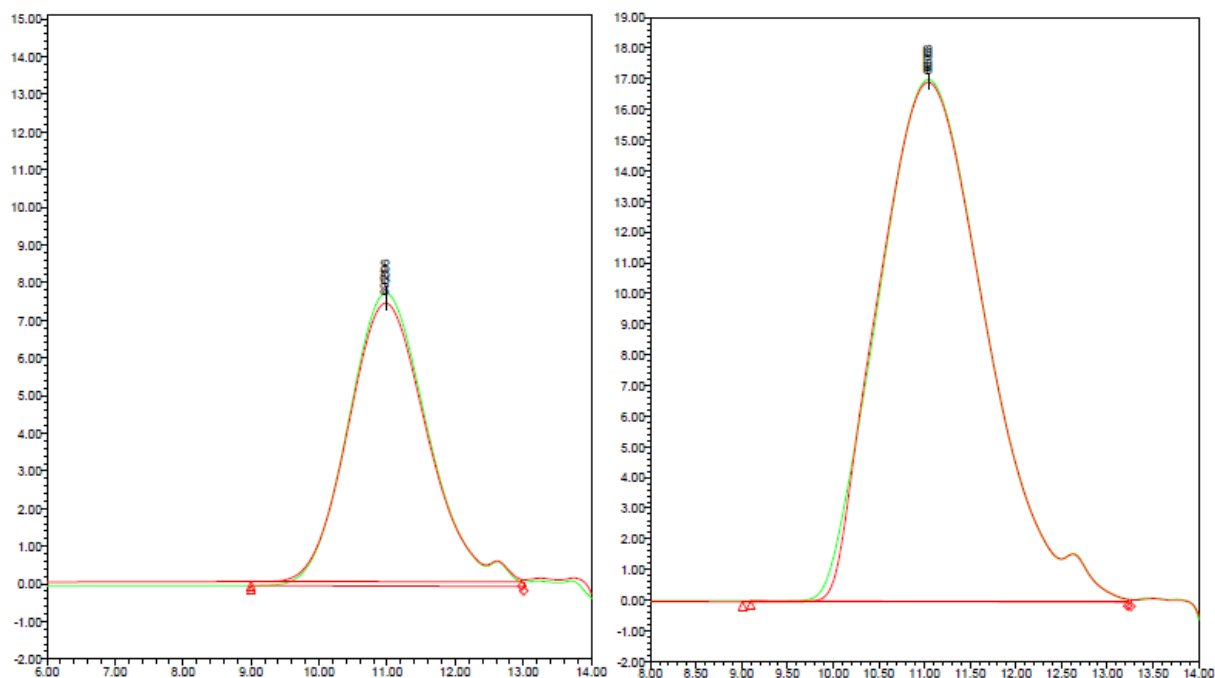


Figure 4: Size exclusion chromatograph results for inhibitor A (left) after autoclaving at 200 °C (green line) and (right) after autoclaving at 250 °C (green line). The red traces correspond to samples that were not thermally treated.

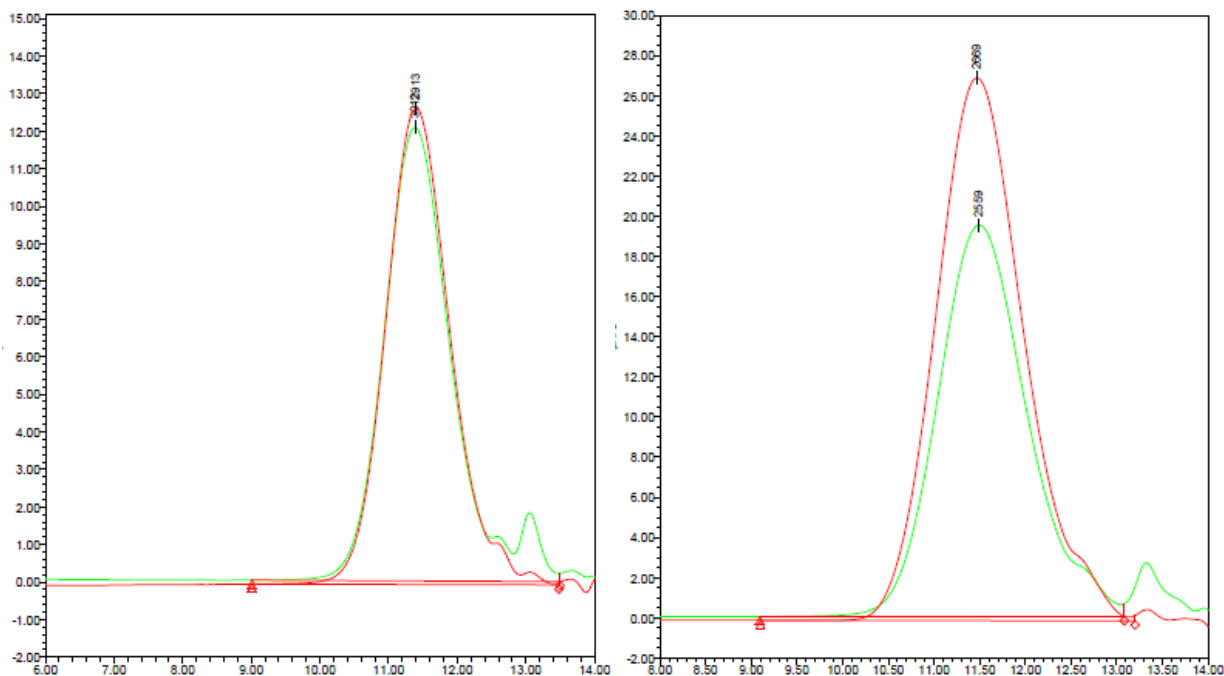


Figure 5: Size exclusion chromatograph results for inhibitor B (left) after autoclaving at 200 °C (green line) and (right) after autoclaving at 250 °C (green line). The red traces correspond to samples that were not thermally treated.

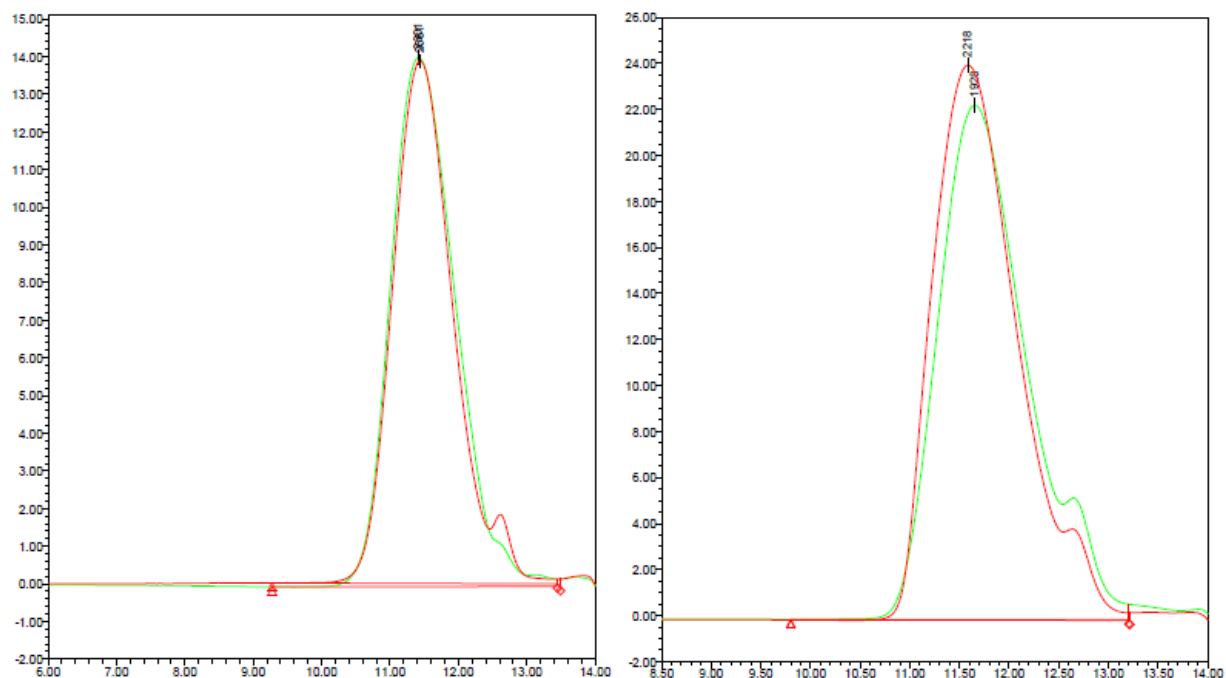


Figure 6: Size exclusion chromatograph results for inhibitor C (left) after autoclaving at 200 °C (green line) and (right) after autoclaving at 250 °C (green line). The red traces correspond to samples that were not thermally treated.

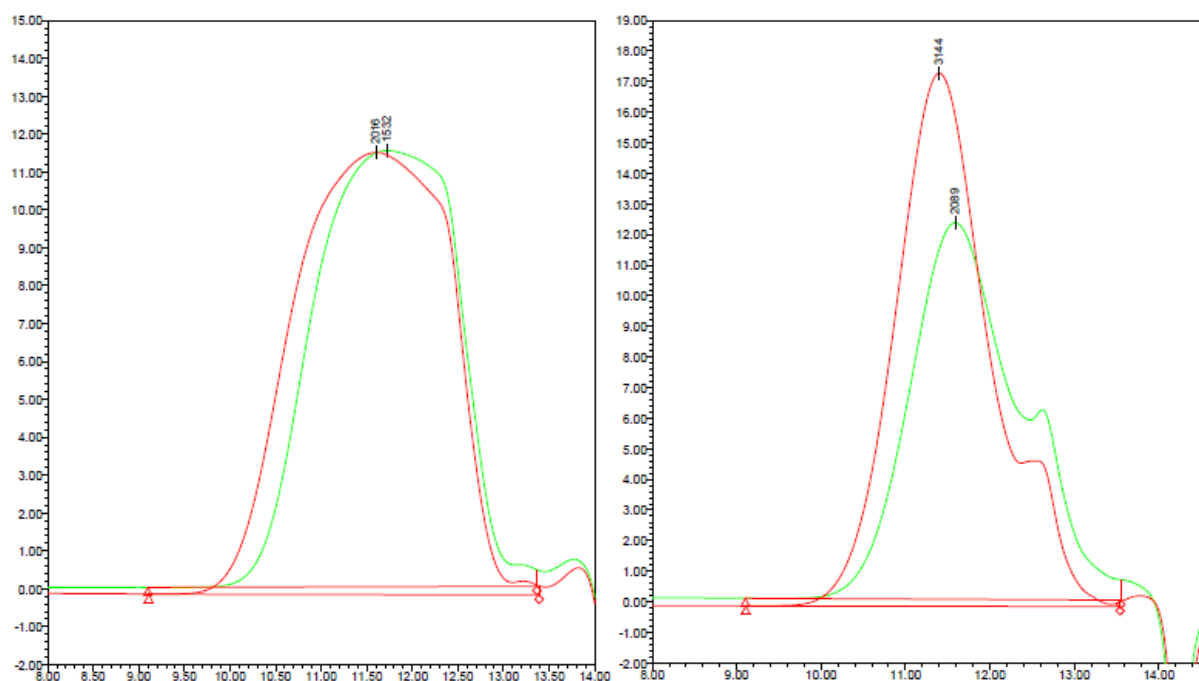


Figure 7: Size exclusion chromatograph results for inhibitor D (left) after autoclaving at 250 °C (green line) and inhibitor E (right) after autoclaving at 250 °C (green line). The red traces correspond to samples that were not thermally treated.



Figure 8: Images of 10 wt.% solutions of (left to right) inhibitor A prior to thermal treatment at 250 °C, inhibitor A after thermal treatment at 250 °C for one hour, inhibitor E prior to thermal treatment at 250 °C, and inhibitor E after thermal treatment at 250 °C for one hour. Note the formation of precipitant in inhibitor E after autoclaving.

3.3 Impact of Aluminum on Calcium Carbonate Inhibition

While the presence of aluminum in geothermal brines is often most apparent in the formation of aluminum silicate deposits, previous testing has indicated that aluminum could also have an acute, negative impact on calcite inhibitor performance (Muller et al., 2018). Furthermore, these initial laboratory results suggested that certain inhibitor chemistries were less vulnerable to “poisoning” even in the presence of 1 ppm of aluminum (geothermal brines typically contain 0.1-1 ppm of aluminum (Amjad et al., 2010)). The goal of this testing was to further this preliminary work by examining the effect of aluminum on additional, thermally-treated scale control products.

The results of calcium carbonate inhibition testing using the NACE synthetic brine with an added aluminum concentration of 0.5 or 1 ppm are summarized in Figure 9. An inhibitor dosage of 5 ppm (as solids) was chosen to maximize differentiation of product performance. For the inhibitor samples that were autoclaved at 200 °C, 1 ppm of soluble aluminum had a modest impact on product performance (15% decline or less), except for inhibitor D, which exhibited a 30% decline in efficacy. Unexpectedly, inhibitor D had the smallest decrease (15%) in calcium carbonate inhibition in the presence of 1 ppm of aluminum after thermal treatment at 250 °C. Inhibitor A also performed well under these conditions with a slightly larger decline in product performance, but yielded a comparable inhibition due its superior “unpoisoned” results. Inhibitors B and C, which were hardly affected by 1 ppm of aluminum after autoclaving at 200 °C, were more acutely impacted by 1 ppm of aluminum after heat treatment at 250 °C (~45% declines in inhibition rates). The effect of 0.5 ppm aluminum, which was only measured with the samples thermally treated at 250 °C, varied slightly amongst the tested antiscalants. However, the two best performing inhibitors, B and C, yielded the highest inhibition results. Additional laboratory testing will be conducted to explore the effects of aluminum poisoning after thermal treatment with the goal of identifying more metal-resistant products.

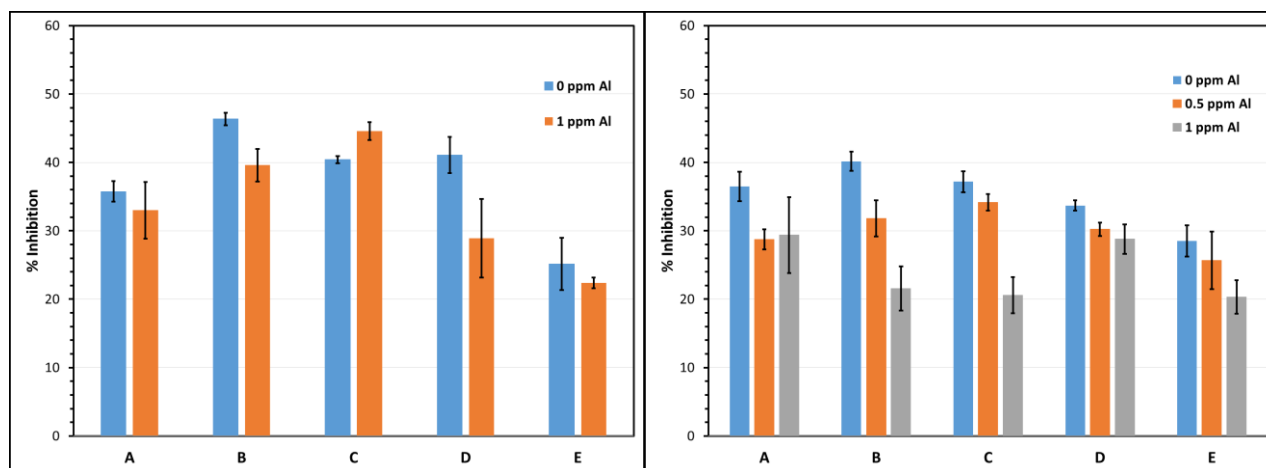


Figure 9: Impact of varying concentrations of aluminum on calcium carbonate inhibition for samples at a test concentration of 5 ppm (as solids). Products were autoclaved at (left chart) 200 °C and (right chart) 250 °C.

3.3 Impact of Iron on Calcium Carbonate Inhibition

Inhibitor samples thermally treated at 200 and 250 °C were also tested for calcium carbonate inhibition in the presence of 1 ppm of soluble iron. While iron is a very minor natural constituent of many geothermal brines (Arnórsson et al., 1983), concentrations of 2 ppm or more have been reported in the Cerro Prieto, Mexico geothermal field (Armienta et al., 2014). The effects of iron on the calcite inhibition performance of the five inhibitors in this study are summarized in Figure 10. Like with the previous aluminum

poisoning tests, the antiscalant dosage was kept constant at 5 ppm (as solids) to try to maximize differentiation in product performance.

In general, 1 ppm of soluble iron was more deleterious than 1 ppm of aluminum under comparable testing conditions. Inhibitor E was especially intolerant towards iron with decreases in inhibition performance of 91% and 81% after thermal treatment at 200 °C and 250 °C, respectively. The other copolymer in this study, inhibitor D, also did not fare well in the presence of iron with declines in efficacy of 72% and 49% after autoclaving at 200 °C and 250 °C, respectively. Lastly, 1 ppm of iron had a similar effect (decreases in inhibition of 30 – 50%) on the three homopolymers, inhibitors A, B and C. These results combined with previous testing (Muller et al., 2018) emphasize the acute impact of ferrous ions on calcite inhibitor chemistries. Furthermore, these findings indicate that for geothermal brines with substantial concentrations of iron, much higher antiscalant dosages may be needed to overcome this iron poisoning effect. The relatively poor performance of the inhibitors in this study in the presence of only 1 ppm of iron also suggest that additional research and development is needed to identify thermally stable, iron-tolerant antiscalants.

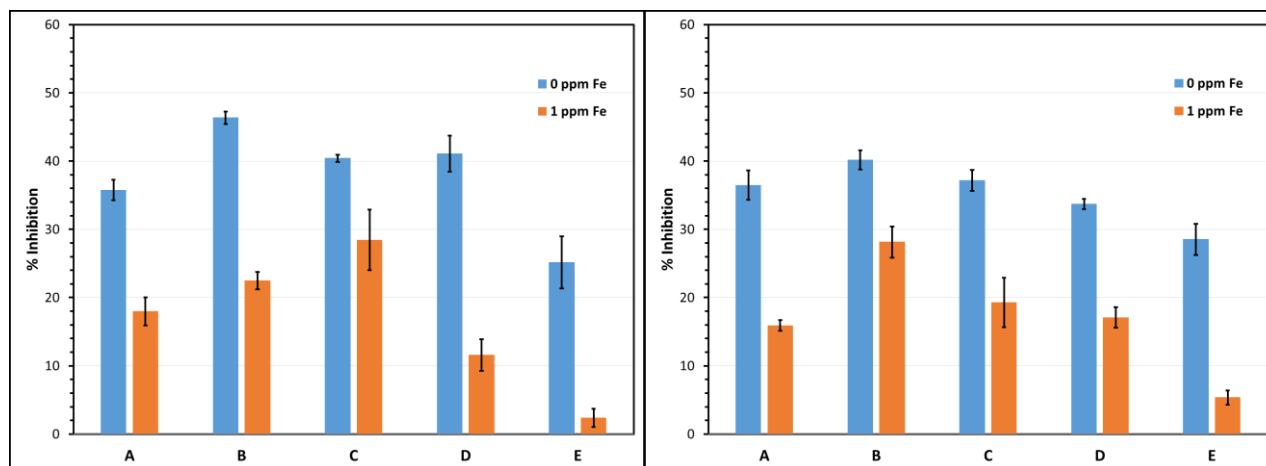


Figure 10: Impact of 1 ppm of iron on calcium carbonate inhibition for samples at a test concentration of 5 ppm (as solids). Products were autoclaved at (left) 200 °C and (right) 250 °C.

4. DISCUSSION

As demonstrated by previous researchers, the standard NACE calcium carbonate inhibition test combined with thermal stability testing was beneficial in screening potential antiscalant products for downhole geothermal applications. Of the five carboxylic acid-based polymers in this study, the homopolymers B and C generally exhibited superior threshold performance, especially when subjected to higher temperature (300 °C) conditions in the GNS Science testing. Differences in the polymeric materials after thermal treatment were also identified via SEC characterization and visual inspection. The two copolymers, inhibitors D and E, exhibited the largest shifts in Mw after autoclaving at 250 °C. These physical changes coincided with declines in calcite inhibition results and suggested that the generation of lower molecular weight materials in these samples negatively impacted antiscalant performance. Conversely, the three homopolymer products produced much smaller shifts in molecular weight distribution after heating, which was consistent with their more robust inhibition performance across the tested thermal treatment scenarios. By combining SEC characterization with performance testing, insights into structure-property relationships for polymeric inhibitors have been obtained. Further analytical testing with additional methodologies, like thermogravimetric analysis/mass spectrometry (TGA-MS), could be utilized to identify thermal degradation byproducts and decomposition mechanisms of these scale control products.

The “poisoning” effect of metal cations on calcium carbonate antiscalants appears to be a largely unexplored topic of research. Previous reports (Zuhl et al., 1987; Amjad et al., 2001) have also demonstrated the acute impact 1 ppm of soluble iron can have on inhibitor chemistries. However, this testing was focused on the effect of ferric ions on calcium phosphate inhibition or iron oxide dispersion under simulated cooling water conditions. Amjad and coworkers (2001) also reported that various copolymers were susceptible to aluminum poisoning at concentrations as low as 0.25 ppm, but this work was again limited to the impact of aluminum on iron oxide dispersion performance. While the three homopolymers in this study largely maintained their effectiveness when exposed to 1 ppm of aluminum after autoclaving at 200 °C, these products were not as robust after the 250 °C thermal treatment. Additionally, 1 ppm of soluble iron proved to be even more challenging with poisoning observed for all of the antiscalants after both thermal treatment scenarios. Discovery of synthetic polymer calcite inhibitors with robust metal cation tolerance and high temperature thermal stability continues to be an ongoing challenge.

5. CONCLUSIONS

While additional systematic research and development is needed to identify more effective geothermal calcite inhibitors, this work demonstrated that metal cations, like aluminum and iron, need to be taken into account when selecting an antiscalant or estimating its dosage. The impact of even minor amounts of these “poisons” could be especially catastrophic when the modeled product dosage is near the threshold concentration for scale control efficacy. Solely utilizing the calcium carbonate saturation index for inhibitor dosage calculations may lead to underdosing, calcite deposition and more frequent wellbore cleanings. This represents an unexpected and unnecessary expense for geothermal plant operators. Furthermore, SEC characterization was identified as a complementary tool to performance testing and a means of quantifying the impact of thermal treatment on polymeric antiscalants. This study identified several polycarboxylate homopolymers that produced robust performance in standard NACE testing, largely independent of exposure to elevated temperatures.

The results from this research project have already been utilized to select inhibitor products for field trials based on the specifics of the geothermal brine chemistry and reservoir temperature. Learnings from these ongoing downhole calcite inhibition trials will be summarized and reported at a future date. Future stages of this research will include measurement of the effect of other contaminants found in geothermal brines, such as manganese, antimony and arsenic. Additional analytical work is also planned to quantify and identify the thermal degradation mechanisms (chain scission, decarboxylation, etc.) that occur within these polymeric inhibitors. Lastly, laboratory research is underway to explore other synthesis techniques to develop thermally stable, high performing calcite inhibitors with improved metals tolerances.

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