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Metal Sulfides and Silicates Inhibition and Impact on Amorphous Silica Scaling

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Keywords

Mineral scaling, amorphous silica, metal silicates and metal sulfides

ABSTRACT

Silica scaling can be considered as one of the biggest challenges in utilizing geothermal energy for electricity production. It is often the thermodynamics of silica saturation that is considered in gauging the scaling tendency of a geothermal fluid. Aside from the thermodynamics, kinetics also plays a significant part and one factor not usually highlighted is the presence of metal ions. Small amounts of highly charged ions can drastically increase the agglomeration of colloidal silica. These ions act as bridges between colloidal silica particles, hastening the growth phase and thus, increasing rate of deposition. An inhibition program that targets both metal sulfide, metal silicate and amorphous silica scaling was tested on a brine from a binary plant. The test was carried out on a sidestream test that mimics the reduction of temperature in a binary plant targeting a silica saturation index of 2.0. Monomeric silica retention was calculated to be around 95% and the scaling spool installed showed minimal adherence of silica for the treated line. Even at the reduced outlet temperature, the deposit weight density is lower for the treated line (38 g/ft^2) compared to the untreated brine at the inlet temperature of 140 deg. C (55 g/ft^2). Exploratory analyses done on the scale deposits confirmed the presence of metal silicates and sulfides for the untreated line. The results of EDS elemental distribution map confirmed that the silica inhibitor program was able to disperse and prevent metal silicate and sulfide co-deposition with amorphous silica. Overall, the monomeric silica retention data complemented with physical observations suggest that the inhibitor program was effective in controlling the scaling even beyond saturation conditions. Actual field applications and trials were also conducted and confirmed that the scale management approach is effective.

1. Introduction

Amorphous silica scaling in different geothermal systems was proven to be a critical limiting factor in achieving operational sustainability. Amorphous silica, including its co-precipitation habits, causes extremely tenacious, highly insulating, and difficult to remove scales (Gill, 2011). In binary cycle geothermal power plants, further extraction of heat from hot brine that causes subsequent cooling leads to silica oversaturation, this condition will contribute to silica scaling which can minimize the heat transfer area of vaporizers and reheaters (Grassiani, 2000).

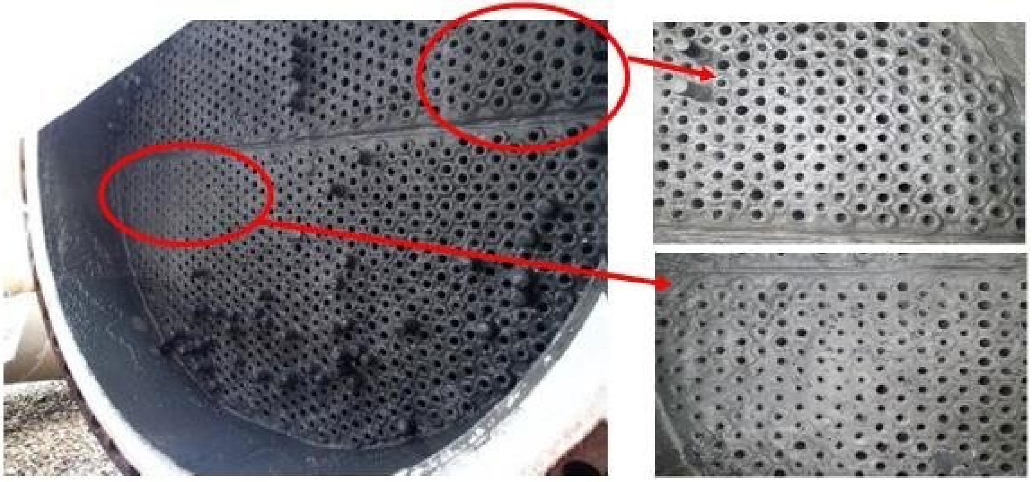


Figure 1: Scaled heat exchanger (vaporizer) tubes that contribute to reduced heat transfer efficiency. (Candido and Zarrouk, 2017)

Currently, there are several methods being used to mitigate amorphous silica scaling in geothermal binary plants. These methods can be roughly categorized as reactive and preventive, both involving mechanical and chemical means. The reactive approach involves cleaning of amorphous silica scales that were already deposited inside the surface pipelines and heat transfer equipment. In an existing binary plant in the Philippines, the proposed cleaning methods were water blasting, mechanical clearing and chemical cleaning using hydrochloric (HCl) acid of hydrofluoric (HF) acid (Candido and Zarrouk, 2017). Water blasting uses high pressure water jet to dislodge deposits that clog the heat exchanger tubes. Mechanical clearing involves the use of drill bit to manually ream the deposits to recapture the capacity of the pipe. Chemical cleaning often involves the use of strong acids to dissolve existing silica deposits. The method is done by recirculating the acid inside the heat exchangers and disposing it through a dedicated HDPE pipe for reinjection. Acid cleaning method was used in binary plants in New Zealand to increase the brine flow. The impact of the cleaning minimizes pressure drop which is indicative of plugging reduction and increasing in temperature difference which means that heat was being transferred from the hot brine to the organic working fluid (Zarrouk, 2014).

Preventive methods for amorphous silica deposition usually involve mechanical reconfiguration and chemical means of inhibition. For binary plants that do not meet the required brine flow by design, residence time inside the heat exchanger unit can be reduced by increasing the fluid velocity of the brine. This can be done by plugging the vaporizer tubes to not more than 10% (Telen, 2015).

Forced precipitation of spent brine using lime was also used in Salton Sea brines (USA). The principle behind is precipitating silica and undergoing clarification before injecting the treated water void of colloidal silica particles. Removal of silica using this method can be lucrative and research is still on-going (Brown, 2013).

In the industry, pH modification of the brine entering the vaporizer is one of the most widely used technique in minimizing the polymerization of amorphous silica; thus, minimizing the deposition tendency. The impact of decreasing the pH of geothermal fluids on silica scaling was documented in different sites (Grassiani et al., 2000). Akaku (1990) documented an acidic well discharge from one production site in Japan where the pH was at 3.9 and has the highest silica concentration among the other wells. This particular well has the least silica scaling compared to the other near neutral wells. A test in Svartsengi (Iceland) showed that spent brine used for power generation from a binary plant did not show any signs of polymerization for 60-80 mins after maintaining it at pH of less than 5.5. In a field test in New Zealand, rapid polymerization was observed at pH of 6 while at pH of 5, no polymerization was observed up to 200 mins. In the Philippines, field test in Mak-Ban geothermal facility used a pH setting of 5.5 to control silica polymerization (Gallup, 1998).

Although effective in delaying the polymerization of silica, Brown et al. (1983) do not recommend injecting the treated fluid because if the induction time is shorter than the perceived residence time downhole, scaling in the wellbore may happen which will plug the reinjection well. In some geothermal systems, scaling of antimony sulfide can be enhanced due to the low pH of the system from acid dosing. Recorded incidents of antimony sulfide scaling in binary plants were documented in Rotokawa and Ngawha (New Zealand) sites (Gill and Jacobs, 2018). Antimony sulfide or stibnite deposits can be tenacious as well and cause fouling of heat exchanger tubes. Aside from the tendency of stibnite precipitation, control of the acid dosing system is critical in achieving desirable results. Based on experience from different fields, insufficient acid dosing can lead to scaling while too much dosing can lead to corrosion and subsequently, surface equipment failure (Gallup, 1998).

The use of polymeric silica inhibitors is gaining interest in the geothermal community because of lower risk compared to pH modification. The challenge now is proving that the solution is technically and commercially viable alternative. Several studies were done to assess the performance of polymeric silica inhibitors. A study by Mejorada et al. (2000) involving a polymeric silica inhibitor was evaluated on a geothermal site in the Philippines. This inhibitor is phosphino-carboxylic co-polymer that was specifically designed to retard silica polymerization. From the results, one ppm of the inhibitor was able to affect the morphology of the scales but was not enough to prevent the deposition completely. It was observed that the polymer was able to prevent the formation of hard, vitreous scales compared to the deposition documented in the untreated line. Another study on this polymer was carried out by Baltazar et al. (2014) in Leyte and Bicol (Philippines) steam fields. Visual inspection proved the favorable performance of the polymer on reinjection pipeline silica scaling mitigation. From the test, it was hypothesized that the proposed mechanism of the polymeric silica inhibitor is to disperse silica colloids – preventing agglomeration and react with corrosion products to minimize monomeric silica deposition.

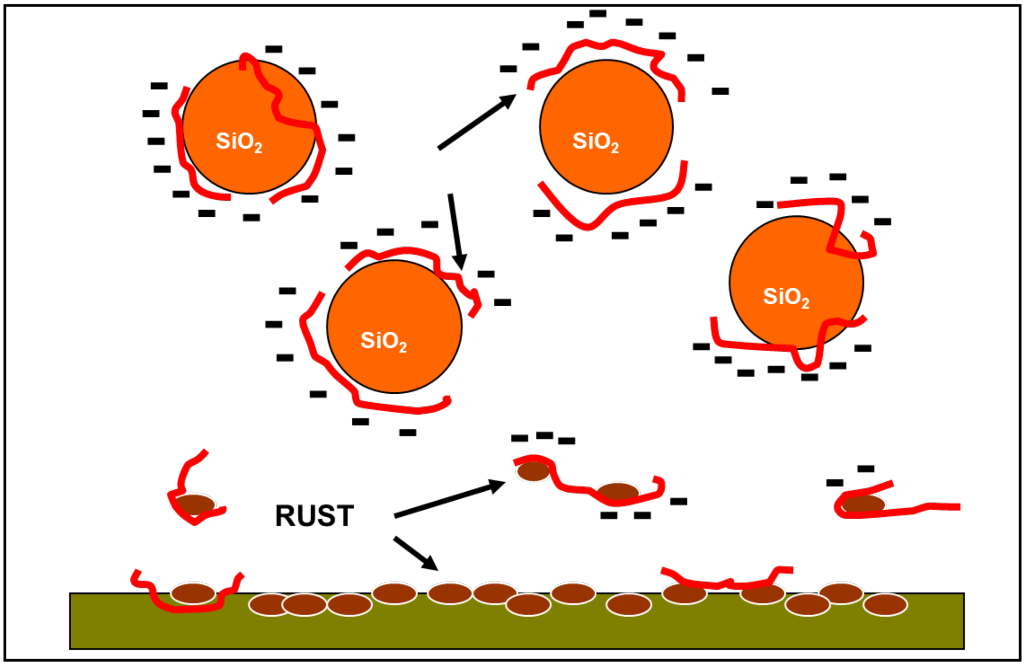


Figure 2: Proposed mechanism of polymeric silica inhibitor in dispersing colloidal silica particles and minimizing monomeric silica deposition (Mejorada et. al, 2023).

The carboxylic groups of the polymer attach itself to the silica molecules giving it a net negative charge which helps in preventing agglomeration and deposition on metal surfaces.
Polymeric silica inhibition studies were also conducted by Gill (2007) in both laboratory and field conditions. The active component of the polymeric inhibitor tested is a copolymer of acrylic acid. From the results of the laboratory tests, the perceived mode of action of this polymer are the following:

- Hydrophobic part of the active molecule prevents direct monomeric silica deposition on metal surfaces
- Acrylic acid helps in attaining a net negative charge among the silica molecules preventing nucleation; thus, polymerization retardation
- The same mechanism also happens with formed colloidal silica particles and in turn, prevents further colloidal particle growth
- Molecular adsorption or complexation also prevents formation of other scale like silicates

Field trials conducted in Heber facility (United States) showed promising results of the inhibitor based on visual inspection and final weights of the scale coupons installed in binary plant inlet and reinjection lines. For Cerro Prieto (Mexico) site, the results of field trial will help evaluate the feasibility of a binary cycle project (Gill, 2011).

Silica inhibition studies in a two-phase header using the same polymer-based inhibitor was also conducted by Jamero et al. (2021) and got promising results based on temperature profile.

In summary, for both laboratory and field trials, results should be evaluated based on monomeric silica levels read using spectrophotometer. Theoretically, yellow molybdate reagent is a colorimetric method that reacts particularly with monomeric silica (Franson, 1985). For inhibition to be deemed effective, the monomeric silica should be retained even past the induction time. Gill (2007) also used pre-weighed scale coupons to quantify the amount of silica formed and adhered on the metal surface. Mejorada et al. (2000) and Baltazar et al. (2014) used pre-weighed inspection spools to capture the amount of deposited silica. The spools are short carbon steel or stainless-steel pipe with 0.5-1-inch diameter. The amount of deposit formed can be used as a starting point to approximate the scaling rate per year. Aside from visual inspection, these measurements provide quantitative approach in assessing the performance of the mitigation technology selected.

Both pH modification and polymer-based silica inhibitors contribute to operational sustainability in terms of potential increase in the electricity generation capacity and preservation of pipeline flowrates (Gill and Jacobs, 2018).
Currently, the most common method being used to push the outlet temperature limitations is pH modification. This involves the use of acid to lower the pH of the geothermal brine, usually at pH 4-5, to delay silica scaling. This can help extract more heat from the inlet brine without causing significant scaling because of the lower outlet temperature setting. Typical challenge with this type of treatment is acid dosing control. In principle, too much acid will result to lower pH which can enhance corrosion of the system causing significant equipment damage. In contrast, too low acid dosing will not maintain the desired pH and will cause scaling.
The use of polymeric silica inhibitors is gaining interest in the geothermal community because of the minimal risk compared to pH modification. In the Philippines, some sites are using polymeric silica inhibitors to mitigate scaling in two-phase pipelines. The same principle can be explored and applied in binary plant operations where silica inhibitor will help extend the SSI operability even at reduced outlet temperatures. With the upcoming planned binary plant expansion facilities in the Philippines, this potential treatment method can be explored as a technically viable alternative to pH modification.

In the absence of an actual binary plant, testing of this potential technology can be challenging. Laboratory test may give idea on the mechanism and kinetics of the proposed solution but the actual field conditions that contribute to scaling propensity might not be factored in. A sidestream silica inhibition test may provide a better understanding of the inhibitor performance. By using a representative fluid from the actual plant, this gives a more approximate condition that can help capture different factors that may affect the performance of the proposed solution. Currently, previous sidestream tests done in the Philippines were either focused on understanding silica scaling behavior in reinjection systems or assessment of pH modification as potential treatment for binary plants. Previous sidestream studies on polymer-based inhibitors were aimed at finding a solution for maintaining reinjection well capacity. These studies only consider retention time and saturation as the dominating factors for scaling.

The study helped in understanding the mechanism of polymer-based scale inhibitors and its applicability on binary plant systems, specifically, the brine conditions similar to observed characteristics in the Philippines. The study also explored the impact of metal silicates and sulfides on the scaling behavior of amorphous silica which is often neglected when managing silica-saturated brines.

2. Methodology

A sidestream silica test skid was fabricated and installed in a binary plant in the Philippines. The schematic setup below outlines the process flow of the proposed study. Main brine inlet of the skid was tapped into the actual binary plant inlet where the incoming stream was divided into two, one is for the treated and the other is for the untreated line. For the treated line, polymeric silica inhibitor program (copolymer of acrylic acid and metal ion dispersant - supplied by Nalco Water) was used. The inhibitor program was composed of two separate chemistries. The silica inhibitor has the following physicochemical characteristics: hydrothermal stability at 320 °C, neat pH at 2.1-5.6, relative density at 1.06 (15.5°C) and kinematic viscosity around 194 mm^2/s (at 20 °C). The metal ion dispersant or metal silicate inhibitor has the following physicochemical properties: hydrothermal stability at 320 °C, neat pH at 2.5-3.6, relative density at 1.113 – 1.149 and kinematic viscosity around 39.93 to 42.69 mm^2/s (at 20 °C).

The separated brine passed through individual coils (internal diameter: 3/8" stainless steel, length: 5.5 meters) where it was cooled to the target temperature of 100°C. An external cooling water supply and recirculation system helped maintain the target temperature and prevented thermal stratification. After reducing the temperature, the cooled brine passed through the retention vessels where the expected holding time was 90 mins. After passing through the retention vessels, the spent brine was collected in a holding tank and was pumped to a nearby sump. Figure 3 shows the proposed schematic diagram of the setup:

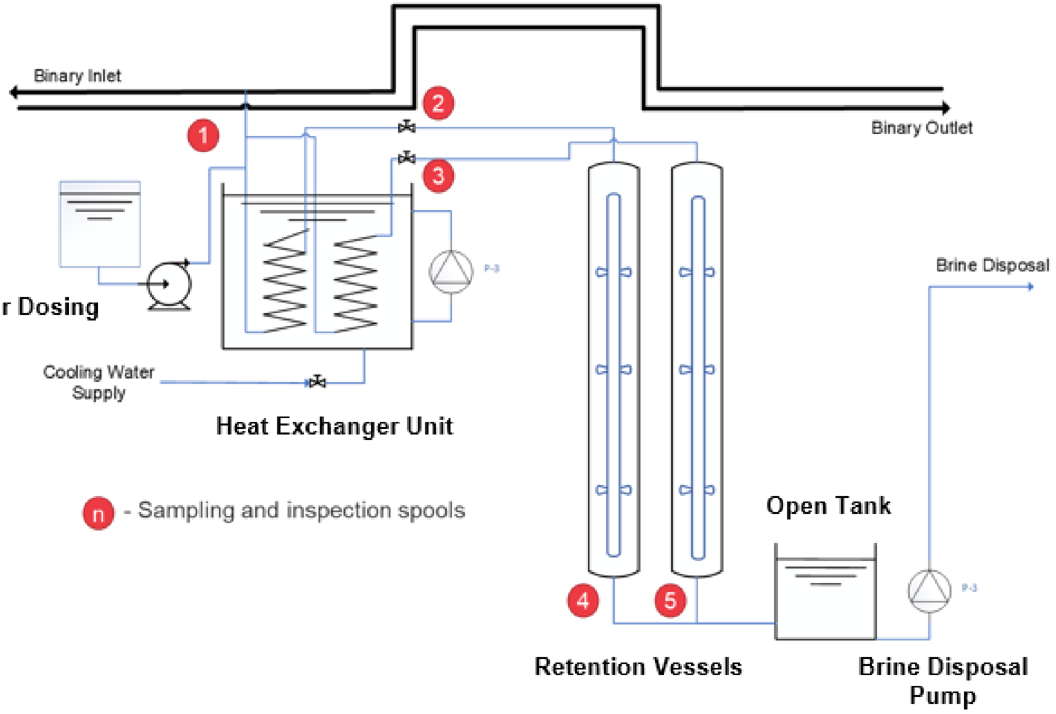


Figure 3: Schematic diagram of the sidestream setup. (The numbers in red circles correspond the location of the brine sampling and inspection spools).

There were five sampling points for water analysis. Inspection spools (1-inch internal diameter and 5 inches length) were used to assess the physical manifestations of scaling,

The trial was conducted for 30 days to capture enough data points for analysis. The parameters that were monitored are the following:

Table 1. Monitored parameters, method of measurement and frequency.

Parameter	Measurement	Frequency
Monomeric silica	ASTM D859-16 (yellow molybdate method)	3x a day 5 sampling points
Pressure	Analog pressure gauge	Manual logging (3x/day)
Flowrate	Ultrasonic flow transmitter (Rosemount)	Logged automatically every 5 mins
Temperature	Temperature probes	Logged automatically every 5 mins
Total silica	Method 6020B - ICP	Once per week (1st and 4th weeks only)

After the 30-day run, pre-weighed installed inspection spools were dismantled for visual inspection and deposit weight density measurement. Retention vessels and baffles were also inspected. Scale samples were submitted to an analytical laboratory in Singapore for XRF and XRD analyses.

For the experimental design, the only setting that was varied was the treatment condition, either treated or untreated. Variations in outlet temperature was minimized by controlling the cooling water supply to keep it constant. This is to maintain a constant silica saturation condition which is primarily driven by temperature. Inlet pressure was also fixed by throttling and adjusting the main isolation valve of the brine supply, thus keeping constant flowrates for both the treated and untreated lines. Dosage for the treated line was maintained at 14 ppm. The dosage was based on Nalco Water Geomizer® modeling software which uses Watch 2.4 speciation software to identify scale forming minerals and the corresponding saturation. The output was used by the modeling software to generate dosing suggestion based on the level of saturation of the brine. Monomeric silica, total silica, pressure, and flowrate were measured for both the treated and untreated streams.

3. Results

Understanding the deposition behavior of silica particles in the trial conditions present can help understand the mechanism of inhibition. The inlet and outlet temperatures were 140°C and ~100°C respectively with pH at around 7. These translate to SSI values of 1.27 and 1.98 (considering 720 ppm actual silica measured at 160-165°C). At these brine conditions where SSI>1.0, nucleation is very rapid (Brown, 2012). Silicic acid molecules form dimers, trimers and so on until increasing to a significant particle size forming a single colloid – hence, the term polymerization. According to Iler (1979), the ionization of polymer species is much higher at pH of 6-7 and above 7 that the polymerization occurs rapidly causing decrease in concentration of monomeric silica. After the initial stages of polymerization, the colloidal silica particles will increase in size which is dependent on the oversaturation of the brine. The agglomeration of silica colloids contributes to surface deposition. According to Brown (2012), silica scaling happens because of interaction between like silica particles. With this condition, it is assumed that a monolayer of silica molecules exists on the surface of the metal pipes where the agglomerated silica particles will attach. The interaction of colloidal silica particles can be calculated with DLVO theory. Normal colloids in solution have a negative charge which causes electrostatic repulsion. As these colloidal particles grow, the distance between particles reduces (in terms of Angstroms) and the stable repulsive electrostatic force turns into attractive London and Van der Waals chemical forces (Brown, 2012). From the studies presented by Iler (1979) and Brown (2012), the hypothesized scaling process inside the pipe involves the following:

1. Formation of iron oxides on the surface of the pipe due to natural flow of geothermal brine and simultaneous slow direct deposition of monomeric silica.
2. In saturation conditions above 1, polymerization of silica happens which will eventually form into colloids and will grow.
3. Due to geothermal brines having high ionic strength, electrostatic repulsion of colloids was reduced, and this enhances the agglomeration of particles. The presence of metal ions also helps in increasing the agglomeration rate of colloid particles by acting as bridge.
4. Particle aggregates will attach to either the iron oxide particles or the slow-deposited monomeric silica. These can serve as either attachment point or seeds for other particles to attach.

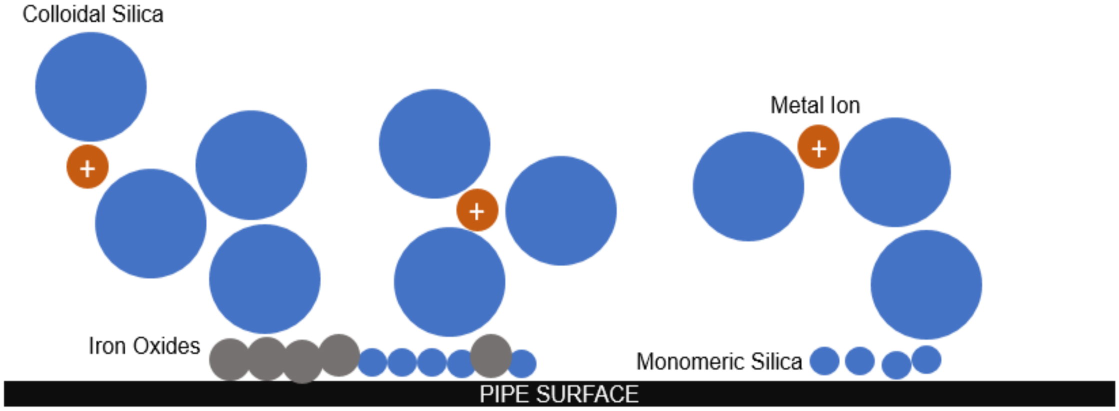


Figure 4: Proposed mechanism of scale deposition on the pipe surface.

According to Gill (2021), functionality of scale inhibitors can be divided into three: threshold inhibition, dispersion, and non-adherence. In the first functionality, scale-forming ions are kept soluble in the solution with the inhibitor being dosed at sub stoichiometric quantities in comparison to the target species. Dispersion functionality works on the particle structure, affecting changes on morphology, size and density, and surface charge. Consumption of inhibitor is significant since this must be adsorbed on the surface of the particles. The last functionality, non-adherence, creates a net negative charge on the particles that will be repelled by the metal surfaces. Based on the inhibitor selection criteria presented by Gill (2021), the most probable modes of action of the polymer-based inhibitor are dispersancy and non-adherence. Based on Gallup (2002), dispersion can be considered as the primary action of successful polymer-based inhibitors. These can impact the scale-forming minerals by increasing the induction period of growth, altering crystal forming habits and reducing potential for aggregation. Brown (2012) presented a mechanism by which dispersion functionality impacts colloid separation. For chemical inhibitors, it is possible that these can increase the energy barrier needed to overcome the electrostatic repulsive forces and turn into attractive forces. The succeeding figure shows the demonstration of the energy barrier increase:

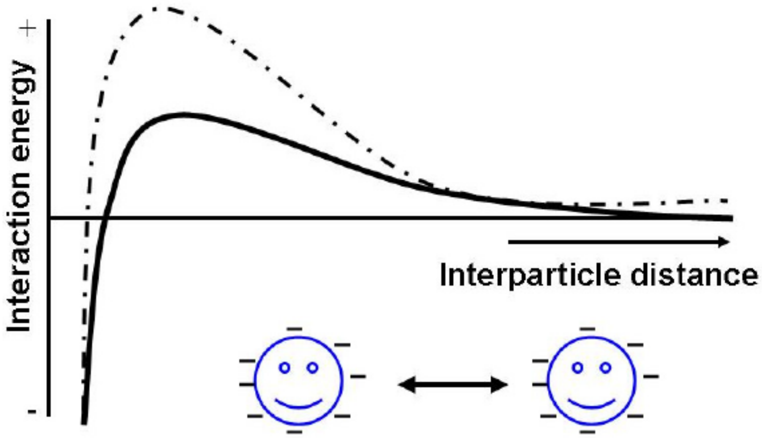


Figure 5: Increase in energy barrier that promotes colloid separation - as illustrated by Brown (2013)

With the learnings from the previous studies by Gill (2011) and Gill (2021), the proposed interactions of the inhibitor program are the following:

1. Affects the polymerization behavior of monomeric silica – results to increase in induction time.
2. Minimizes adherence of monomeric silica on pipe surfaces.
3. Enhances the electrostatic repulsive forces on colloidal silica particles by increasing the needed interaction energy to reverse these forces
4. Minimizes agglomeration of colloidal silica particles by effecting a net negative charge
5. Disperses metal ions by changing the surface charge to prevent it from acting as bridge between colloidal silica particles.

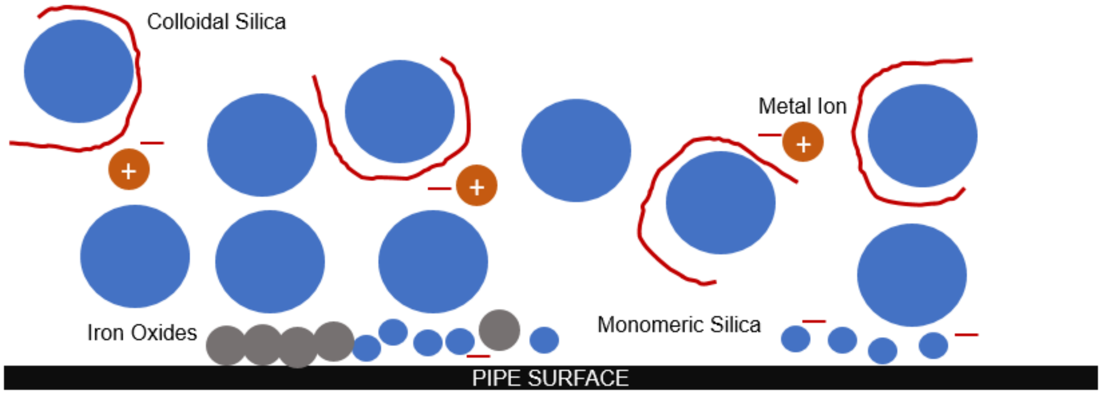


Figure 6: Interactions of polymer-based inhibitor on monomeric, colloidal silica and metal ions in the system.

An important response that was measured during the trial was monomeric silica which was measured based on ASTM D859-16 (yellow molybdate method). For the trial, the measurement was done using a spectrophotometric determination of molybdate-reactive silica in the brine sample. The molybdate-reactive silica can be in the form of simple silicates, monomeric silica and silicic acid which are often referred to as reactive silica. Hach® high range silica reaction pillows were used, and the samples were read using Hach® DR900 multiparameter portable colorimeter.

Figure 7. Hach® silica high range reagents and Hach® DR900 portable colorimeter were used to monitor the monomeric silica levels.

For the analysis, a 1-mL brine sample was taken from the target sampling line and was diluted to 10 mL. The molybdate reagent will then react with monomeric silica in the brine sample forming a distinguishable yellow complex. The intensity of complex will be read against the original sample serving as blank.

There were five sampling points used to monitor the monomeric silica levels of different streams to determine how much was retained. The inlet brine monomeric silica level will serve as a baseline for both the treated and untreated lines. Samples were also taken after the cooling coils which captured the impact of temperature decline on monomeric silica retention. Furthermore, samples were also collected after the retention vessels to determine the impact on monomeric silica after holding the brine past its projected induction time.

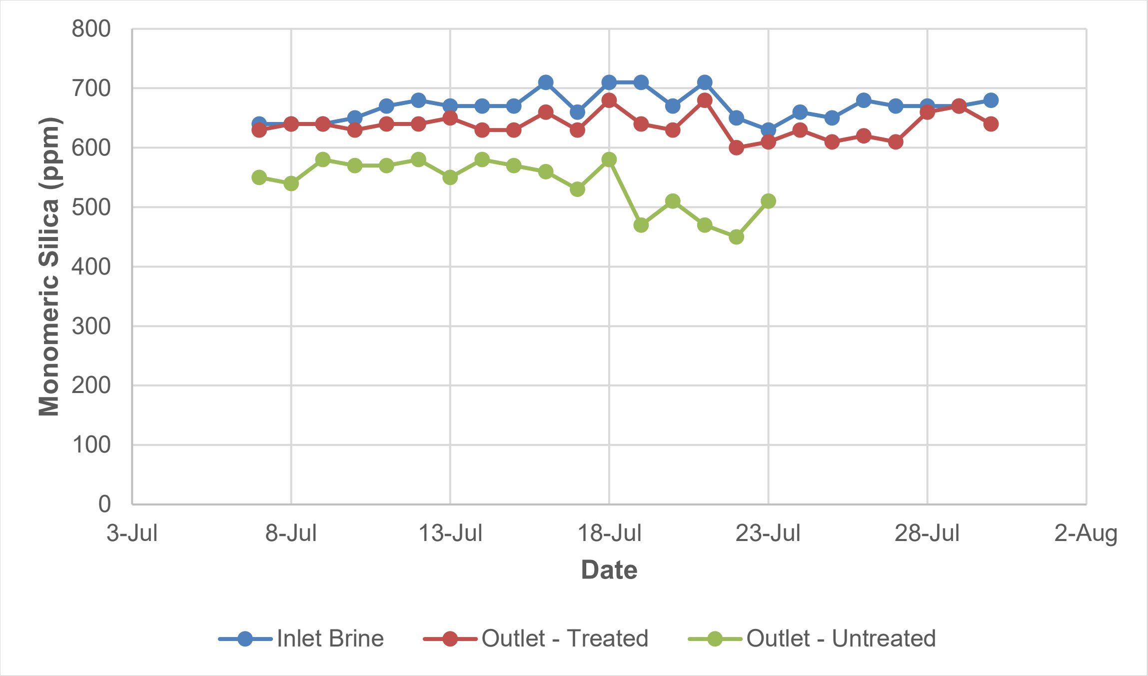


Figure 8: Monomeric silica readings of inlet brine, treated and untreated outlet streams after cooling to around 100 °C.

Using the average monomeric silica level of the inlet brine as the benchmark, the calculated percent monomeric silica retention for the treated and untreated lines were 95% and 80% respectively (using reduced data points for the untreated line). The monomeric silica trend observed on the treated line complements the proposed mechanism of inhibition. It can be noted that the inhibitor generally affected the polymerization behavior of monomeric silica; thus, keeping it soluble in the solution. Aside from the effect on monomeric silica, colloidal silica interaction leading to scaling was also reduced considering there was no significant drop in total silica (Table 2).

The attained monomeric silica retention for the treated line was higher than the target set by the plant which is at least 90%. Two-sample t-test between the treated and untreated monomeric silica levels was also done. The means of the two data groups were significantly different.

Aside from the effect of reduced temperature, there was also a significant impact on monomeric silica retention after holding the brine beyond its induction time. Figure 4.19 shows the monomeric silica levels at the inlet and outlet of the retention vessel.

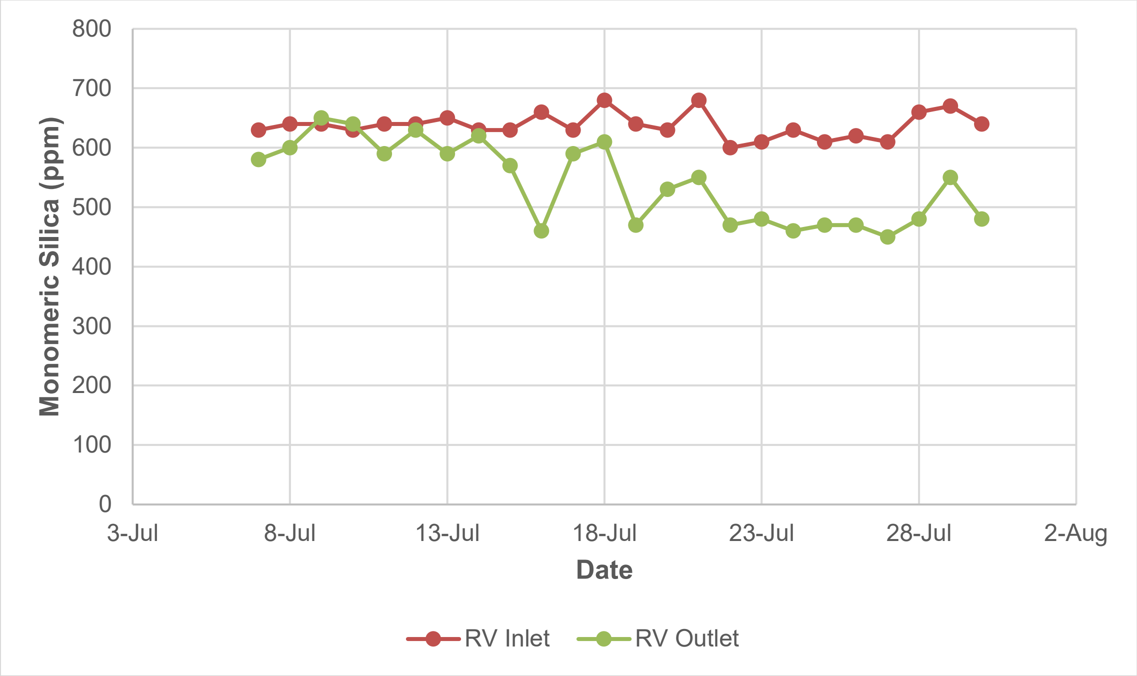


Figure 9. Monomeric silica levels before and after holding the brine in the retention vessel.

Using the average values of the inlet and outlet monomeric silica levels, the projected percent retention was around 80%. For the untreated line, even with the reduced data points, the calculated percent monomeric silica level was around 70%. If the same benchmark of 90% monomeric silica retention will be used, the value obtained for the treated line may not be favorable, but the longer retention time should be taken into account. A study done in Kizildere geothermal field in Turkey captured the trend of monomeric silica levels with respect to pH and time.

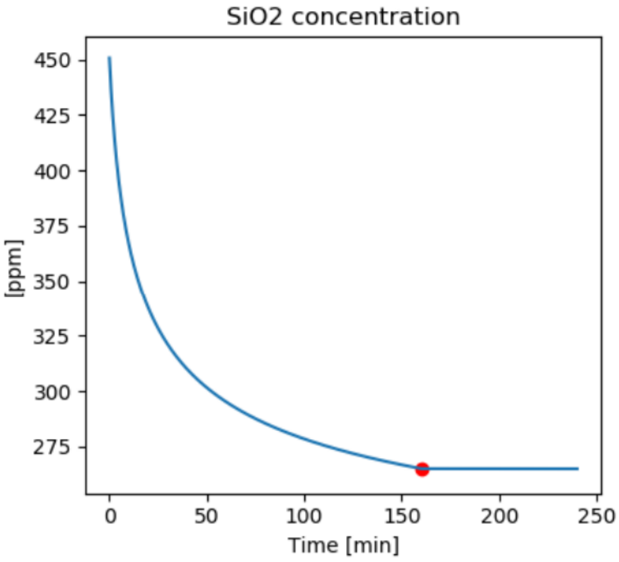


Figure 10: Trend of monomeric silica level versus time at pH of 7 and temperature of 50°C. (Pardelli et al., 2021)

It can be observed that time is a crucial parameter because aging geothermal fluids allow the polymerization of monomeric silica in excess of the equilibrium amorphous silica concentration. Longer retention time significantly decreased the monomeric silica concentration up to the equilibrium concentration. It can also be observed that monomeric silica levels will not fall below the equilibrium concentration despite holding the brine for longer periods of time hence a constant level after reaching the equilibrium concentration (Pardelli et al., 2021).

The reduced brine flow significantly increased the retention time towards the end of the trial. Plotting the monomeric silica levels at the treated line retention vessel outlet against the projected retention time based on flowrate, the observed trend is shown in Figure 11.

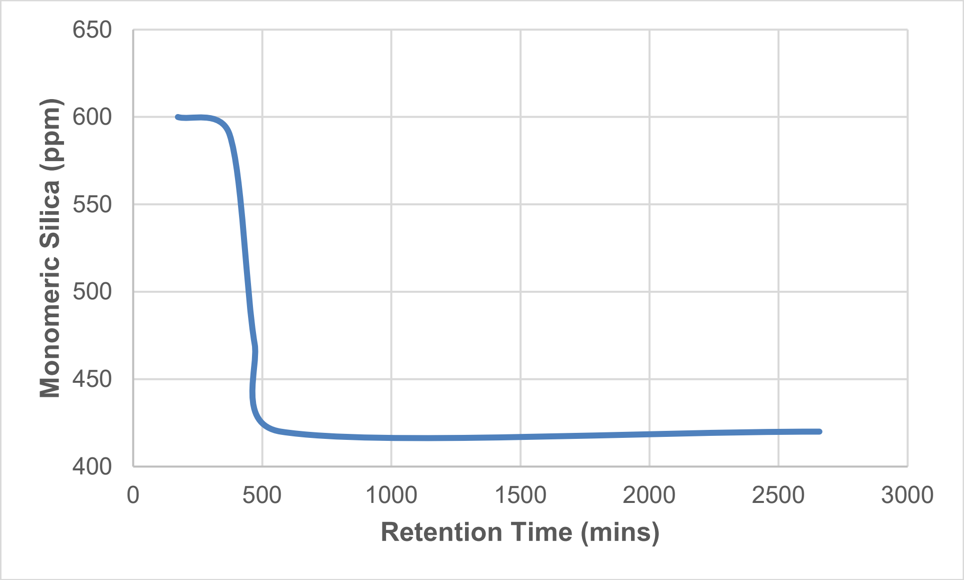


Figure 11: Treated line outlet monomeric silica levels at varying retention time.

Based on the obtained trend, it will take around 373 minutes before the monomeric silica will start to decline significantly. Iler (1979) also observed a drastic decline in monomeric silica past the induction time which was described as autocatalytic. Monomeric silica levels will stay constant despite the increased retention time once the equilibrium was reached based on solution temperature. The same general trend was observed in the study of Pardelli et al. (2021). It can be observed that the inhibitor can keep the monomeric silica soluble at 100 °C outlet temperature for more than 90 minutes. This means that even at the reduced temperature, the brine has enough travel time from the outlet of the binary plant to the target reinjection well.

Aside from monomeric silica, brine samples during the first and last weeks of the trial were sent to Nalco Water Analytical Laboratory in Singapore for ICP analysis. Ten mL of brine sample was diluted to 100 mL and was acidified by adding nitric acid until reaching a pH of 1.5. This will help delay polymerization while the sample is in transit. The total silica levels are summarized in the succeeding table:

Table 2. Total silica levels during the first and fourth week of the trial.

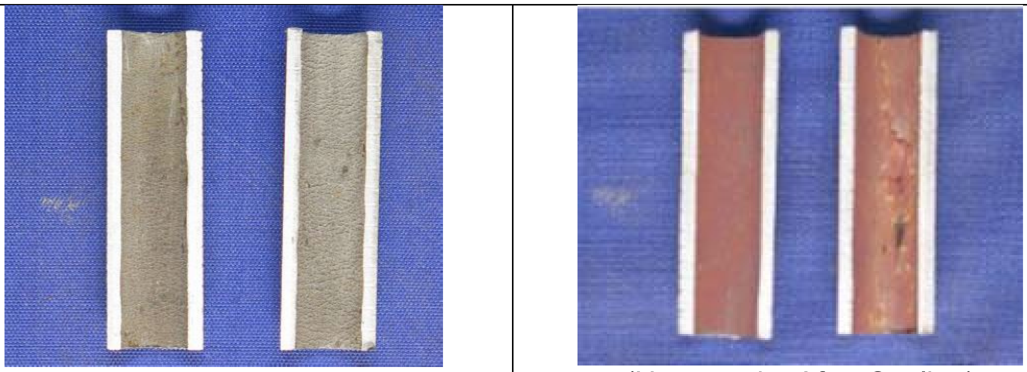
Sample	Inlet (ppm)	Treated (ppm)	Untreated (ppm)	Retention Vessel – Treated (ppm)	Retention Vessel – Untreated (ppm)
1st week	720	710	650	650	600
4th week	720	680	190	630	170

The results of the total silica during the last week of the testing further affirms that there was flow stagnation. If the stream of the untreated line is still flowing, the total silica in the system should still be close to the total silica during the first week. Significant decline in total silica for the untreated line means that the monomeric silica has already polymerized, formed colloidal particles and eventually, may have been co-deposited as iron silicates. The stagnation of flow may have depleted the monomeric silica in the system below the projected equilibrium concentration of ~364 ppm around 100°C.

3.1 Spools and Retention Vessels Inspection

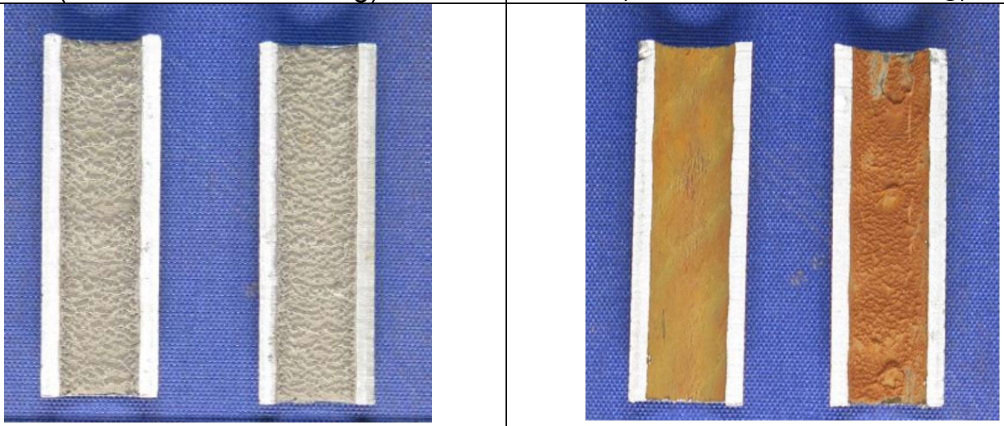
The inspection spools used in the trial were submitted to Nalco Water Analytical Laboratory in Naperville, Illinois for deposit weight density measurement. Figures 12 and 13 summarized the condition of the inspection spools upon analysis.

Figure 12. Internal condition of the inspection spool installed in the inlet stream.



(Treated – After Cooling)

(Untreated – After Cooling)



(Treated – After Retention Vessel)

(Untreated – After Retention Vessel)

Figure 13. Comparison of treated and untreated inspection spools installed after cooling and after the retention vessels.

Physical observations of the inspection spools for both the treated and untreated lines were consistent with the initial inspection of the cooling coils. Characteristic manifestation of surface corrosion was observed in the untreated line while the thin layer of deposits was observed on the surface of the treated line. The measured deposit weight density is summarized on the table below:

Table 3. Deposit weight density measurement of the spools.

DWD (g/ft^2)	**Inspection Spool Location**				
Pipe Side	**Inlet**	**Treated (after cooling)**	**Untreated (after cooling)**	**Treated (after RV)**	**Untreated (after RV)**
Lower	35	22	18	84	15
Upper	20	16	7	82	7

(Narayanan, 2022) – Nalco Water Analytical Laboratory – Naperville, Illinois

Generally, a higher deposit weigh density (DWD) means that there are more scales per unit of area in the pipe. In this case, the DWD values obtained from the untreated line cannot be used for comparison since it was observed that there was flow stagnation in the line that contributed to the depletion of monomeric silica; thus, having minimal deposits. The deposits measured in the treated RV spool was significantly higher than the spool after cooling because the retention time was more than the target 90 mins. Using the trend observed in Figure 11, significant decline in monomeric silica was observed past 373 minutes, this has favored colloidal silica formation, agglomeration of particles and deposition on the pipe surfaces. For the inspection spools after temperature reduction, possible impact on scaling tendency due to rapid cooling can be considered negligible. According to Brown (2012), rapid cooling of brine causes small colloidal silica particles and the corresponding deposition will be lesser. This rapid cooling should happen in matter of seconds. For the sidestream test, the temperature reduction happened within 3 – 5 mins, consistent to the projected time in the actual plant. This cooling time disregards the possible false positive outcome because of reduced colloidal silica size.

A helpful use of the DWD data obtained is the comparison of the inlet and treated line inspection spools. It can be observed that even with the increased saturation resulting from the decrease in temperature, the amount of deposits was lower in the treated line compared to the inlet line. This may suggest that the polymer-based inhibitor was effective in minimizing the deposition despite the increase in saturation.

However, the deposits on the internal surface of the spools were subjected to X-ray fluorescence (XRF) analyses to get further information on the elemental distribution. The XRF comparison of each spool deposit is shown in Figure 14.

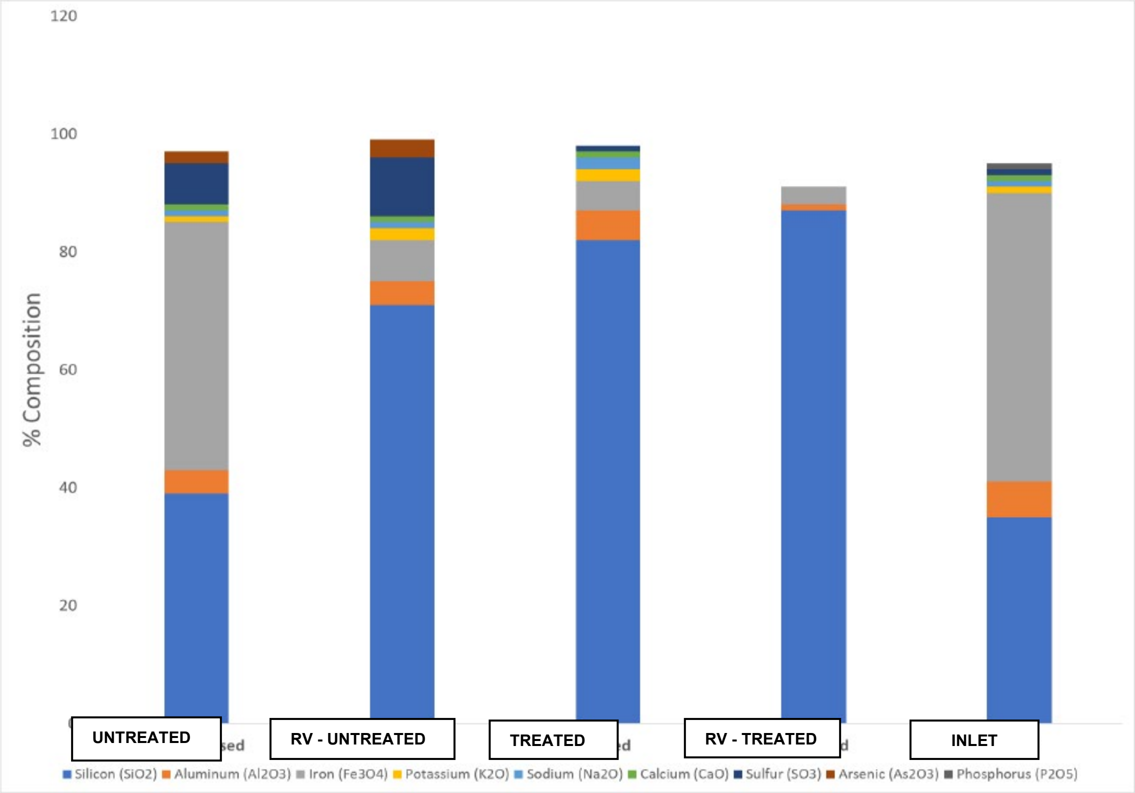
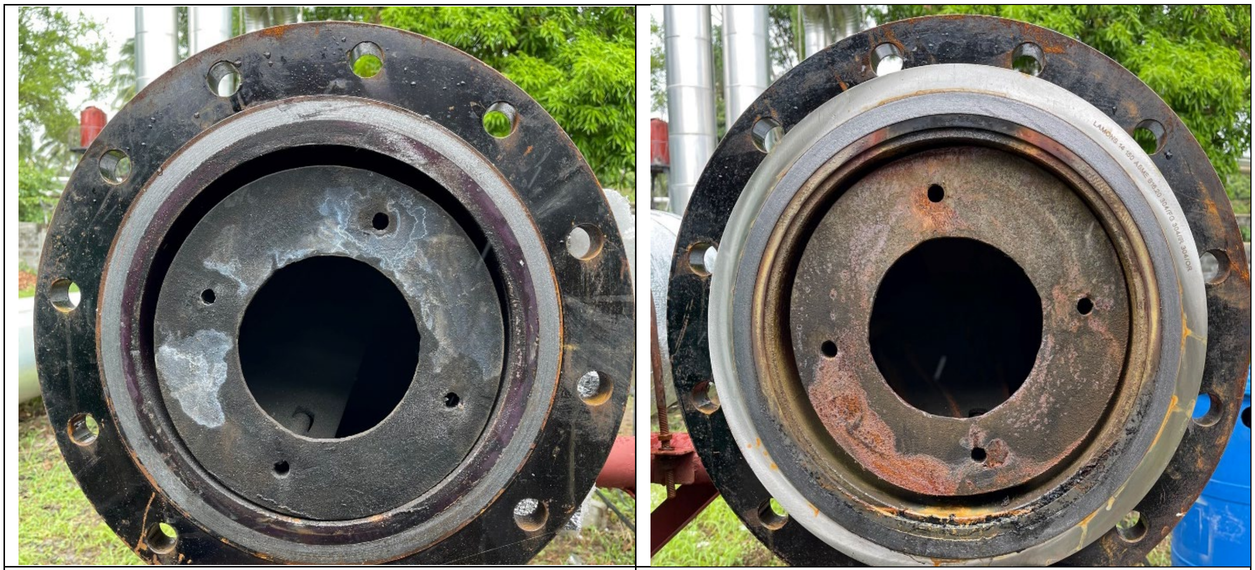


Figure 14. XRF analyses of the deposits found on the surface of the spools.

It can be observed that majority of the scale composition of the treated line was amorphous silica while the untreated and inlet lines was iron. Sulfides in the deposit was also significant in the untreated line. There is also a considerable percentages of metal ions in both the untreated and inlet lines. This observation further validates the metal silicate inhibition capability of the polymer-based inhibitor used.

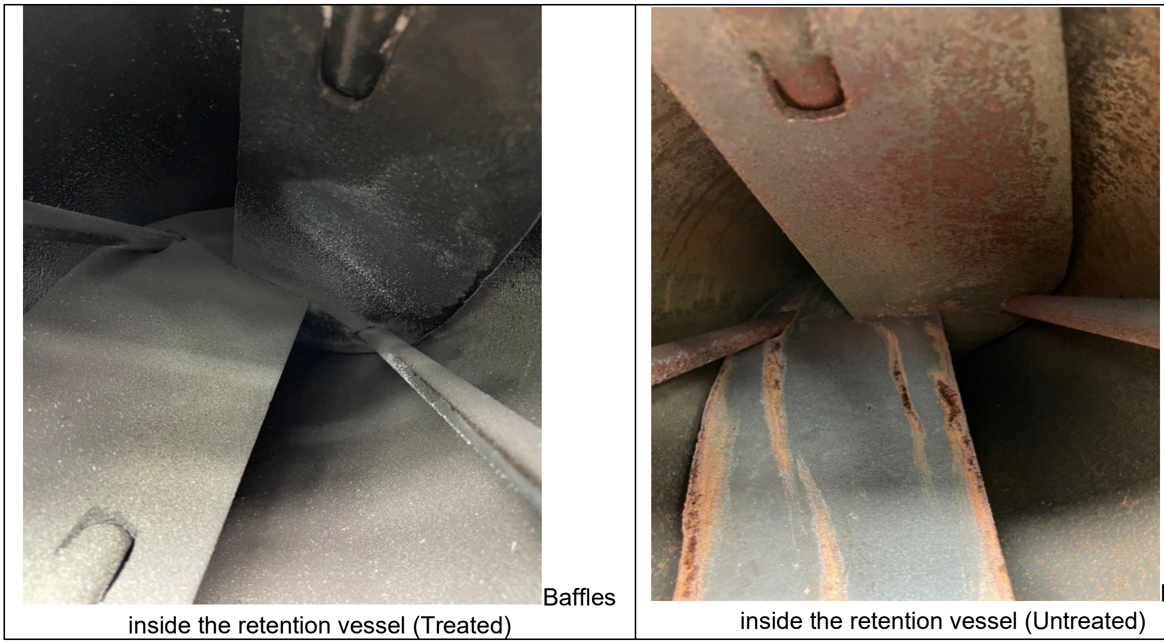
The inspection of the retention vessel of the treated line also showed minimal adherence of scale on the surface. Like the cooling coils and inspection spools of the untreated line, general corrosion was observed on the surface for both the vessel and the baffles.



Opening of Retention Vessel (Treated)

Opening of Retention Vessel (Untreated)

Figure 15. Inspection of the retention vessels after the 30-day run.



Baffles inside the retention vessel (Treated)

Baffles inside the retention vessel (Untreated)

Figure 16. Internal view of the baffles before pull out.

Scale samples were obtained by scraping the surface of the baffles. These were sent to Nalco Singapore lab to confirm the composition and structure. From the results of the XRF and XRF analyses, the dominant scale type on the treated line surfaces was amorphous silica with confirmed traces of magnetite. For the untreated line, majority of the deposits was iron silicates, amorphous silica and confirmed formation of hematite. The results of the XRF and XRD were consistent to the deposit analyses done on the inspection spools internal surfaces.

To explore the metal ion dispersion capability, an energy dispersive spectroscopy (EDS) was conducted on the adequate deposit samples found on the surface of the treated and untreated retention vessel inspection spools.

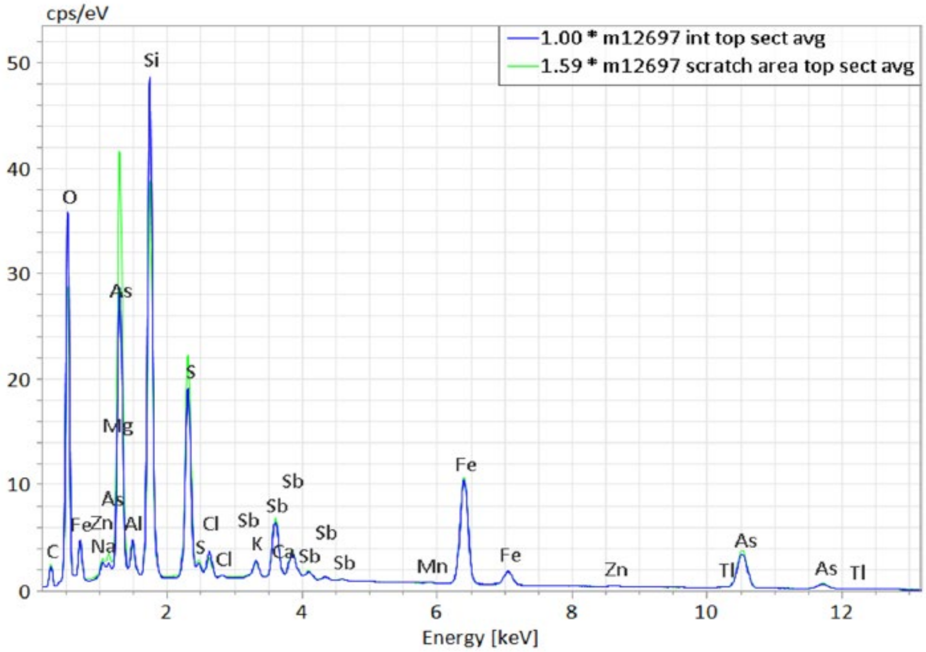


Figure 17: Elemental distribution map of the untreated RV inspection spool.

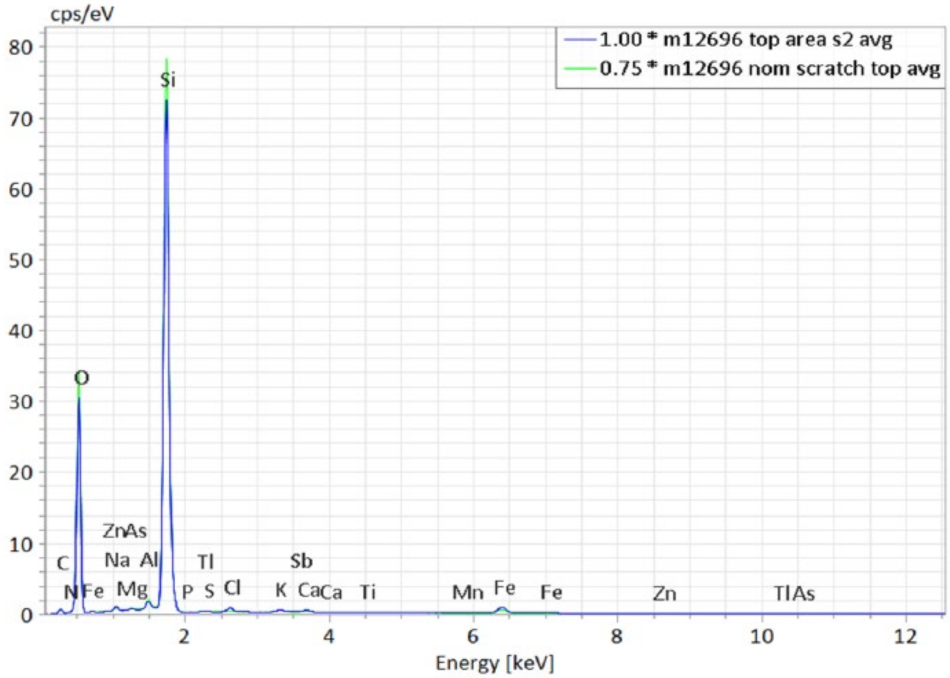


Figure 18: Elemental distribution map of the treated RV inspection spool.

The distribution map of the untreated deposit sample shows considerable peaks of metal ions like magnesium, aluminum, and iron. Toxic elements like arsenic and aluminum were also co-deposited with amorphous silica. A peak in sulfur was also observed which may indicate metal sulfides in the scale. Elemental distribution map of the treated deposit sample shows silica as the major composition. Very low peaks of metal ions were observed which confirmed the dispersive capability of the inhibitor.

4. Summary

The main objective of the study is to evaluate a potential alternative for minimizing potential scale deposition in above-saturation binary plant conditions. This was done by fabricating a setup that can mimic the reduction in brine outlet temperature because of heat extraction. Consequently, holding the brine for a specific period was also done to simulate the travel of the brine from the outlet of the binary plant to the target reinjection well. The setup was able to reduce the outlet temperature of the treated and untreated lines close to the target value. Unfortunately, the brine flow going to the skid was erratic and gradually reduced because of pressure build-up and preferential flow to the main line. Since the retention time was based on the design flowrate, the projected holding time for the brine was increased to up to 2658 minutes. This was significantly longer than the target 90 minutes retention time.

The study utilized different information available to assess the performance of the polymer-based silica inhibitor. From the results of monomeric silica retention data from the dosed line, it showed the inhibitor program is effective in maintaining monomeric silica at around 95%. The achieved percent retention is promising in comparison to the empirical data obtained from different geothermal treatment sites. Examination of the inspection spools installed at the brine inlet and treated line cooling coil outlet showed minimal adherence of silica on the surface of the pipe. Even at the reduced outlet temperature, the deposit weight density is lower for the treated line (38 g/ft2) compared to the untreated brine at the inlet temperature of 140 deg. C (55 g/ft2).

The flowrate readings during the trial were lower than expected because of throttling due to limited cooling water supply. The impact of this was on the retention time which is longer than the projected 90 mins. At a much harsher condition, the dosed line monomeric silica retention after the holding vessel registered at around 81%.

Unfortunately, the untreated line cannot be used as a direct comparison because of the low velocity condition that occurred. The sudden spike in outlet pressure signaled an obstruction or deposition along the lines and the inspection after the trial confirmed the unforeseen condition. The presence of characteristic general corrosion and lower than equilibrium concentration total silica confirmed the flow stagnation. This has reduced the data points used for the untreated line monomeric silica readings and the deposit weight density measurement. Using the available data, the projected percent monomeric silica retention for the untreated line was at 80%.

Exploratory analyses done on the scale deposits confirmed the presence of metal silicates and sulfides for the untreated line. The results of EDS elemental distribution map confirmed that the polymer-based silica inhibitor was able to disperse and prevent metal silicate and sulfide co-deposition with amorphous silica.

Overall, the monomeric silica retention data complemented with physical observations suggest that the inhibitor program was effective in controlling the scaling even at a reduced outlet temperature.

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