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Multi-Method Approach in Addressing the Potential Scaling Problem for the Proposed Brine Optimization Plant at Mt. Apo Geothermal Project

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ABSTRACT

Development of a brine optimization plant is being explored in Mt. Apo Geothermal Project (MAGP), utilizing existing geothermal fluids to generate additional power without having to drill a new well. Silica fouling (scaling) is a common occurrence in a binary plant since its solubility is largely dependent on temperature, among other factors. Aside from amorphous silica, other scales have the potential to form mainly caused by brine cooling that could damage and foul the heat exchangers, pipelines and wellbores. Installment of a proper scaling inhibition system, that is thoroughly studied, will be necessary to address these potential problems.

This study presents the results of a series of tests, from laboratory tests and tabletop geochemical modeling, to field tests, to simulate process conditions of the utilized brine. The two chemical methods that were investigated to inhibit silica polymerization are pH-modification using acid and silica colloidal dispersion using a chemical inhibitor. The results showed that pH-modification (lowering of pH from ~7.3 to 4.7 via acid-dosing) is the more effective method in solving the scaling problem for the MAGP binary project. The silica trends are consistent with the visual inspection and petrographic results, indicating that pH-modification is an effective solution to retard precipitation and deposition of amorphous silica inside and further downstream of the binary plant. However, corrosion risk accompanies the pH-mod method, so a robust, auto-response, acid-dosing system is needed to avoid either over-dosing or under-dosing of acid that on the other hand, can result to massive scaling.

1. INTRODUCTION

Mt. Apo Geothermal Project (MAGP) is located at the northwestern flank of Mt. Apo in the island of Mindanao, Philippines (Figure 1). MAGP hosts a liquid-dominated geothermal system, where two production sectors are present, namely, Sandawa and Marbel. The former is characterized by reservoir temperatures of greater than 300°C, forms the upflow region of the geothermal region and hosts some wells that discharge acidic fluids (as low as pH 2), while the latter has lower reservoir temperatures of around 240 to 260°C, and hosts neutral-pH reservoir fluids.

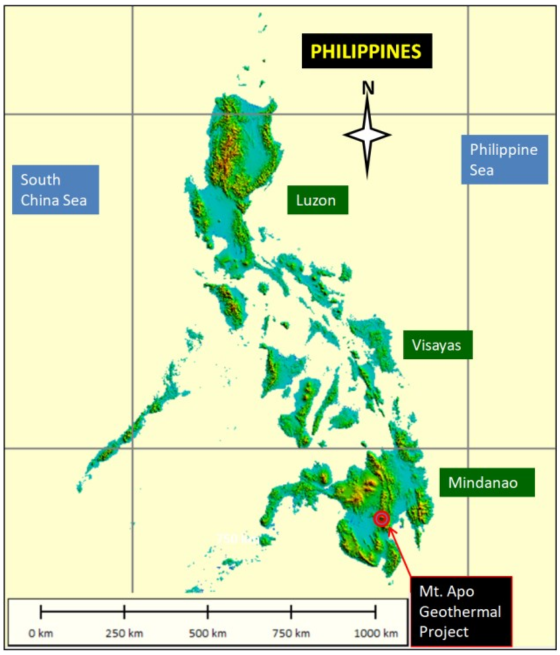

Figure 1. Map showing the location of Mt. Apo Geothermal Project (MAGP) in the island of Mindanao in the Philippines.

A brine optimization plant (organic rankine cycle) is being proposed in the Mt. Apo geothermal field to utilize brine from Marbel sector. A binary-type power plant uses high-temperature brine fluid as heating media for a secondary working fluid (typically an organic substance that has a low boiling point such as isopentane) (DiPippo, 2016). Putting up a binary plant in an operating geothermal field comes with risks that may affect its facilities and geothermal resource. One of the major risks is the deposition of scales in heat exchangers, wells, and pipes which may hinder the operations. This study primarily focused in controlling the precipitation of silica, which is one of the most ubiquitous and troublesome mineral scales in geothermal power generation and injection facilities (von Hirtz, 2016).

Silica exists in a number of different forms, and the form of silica normally precipitated at the surface is amorphous silica. As is the case of most minerals, its solubility is largely dependent on temperature and is given by this equation (Fournier and Rowe, 1977):

$$\log C = -731/T + 4.52;$$

where C and T are silica concentration (mg/kg) and temperature (Kelvin), respectively. The solubility of quartz and amorphous silica as a function of temperature is shown in Figure 2. Included in the figure are the actual silica concentrations along the MAGP brine line as it progresses from the low pressure station (LPBL) to the projected location of the binary plant (ORC) and reinjection well (RIW). Downstream of LPBL, the brine temperature is at ~150 °C with silica concentration of ~580 ppm, which is equivalent to silica saturation index (SSI) of roughly 1.0, with neutral pH.

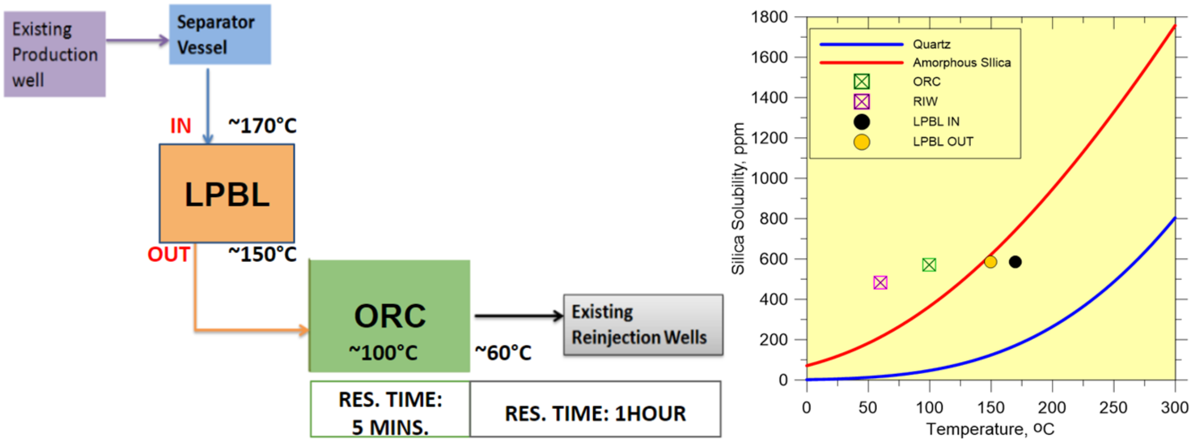

Figure 2. Left figure is a schematic diagram of the projected path of Marbel brine upon commissioning of the binary (ORC) plant. In the right figure, silica concentrations of the Marbel brine overlain in the silica solubility curve of Truesdell and Fournier (1976).

Within the binary plant, the temperature of the brine will initially drop to 100°C, and exits at an outlet temperature of as low as 60°C (Figure 2). Because of the change in temperature, silica solubility will be reduced as shown in Figure 2 with SSI values of 2 to 3, hence scaling may be inevitable within the ORC components, along the brine line and down to the injection wells, if the Marbel brine is not chemically treated. That is why an effective silica inhibition system is vital to avert scaling problems that may trigger emergency shutdowns and well acidizing or work-over jobs, incurring considerably high costs. This study also tackles other potential mineral scales such as stibnite and anhydrite in later sections.

Two chemical methods were investigated to inhibit silica polymerization namely, pH-modification using sulfuric acid (lowering of pH), and silica colloidal dispersion using a chemical inhibitor. This study focused more on the former in the preliminary stages of testing, while the latter was only included in the pilot testing in the field. The pH-modification process is a proven cost-effective method to control scaling in the geothermal industry (Gallup, 2011).

2. METHODOLOGY

Evaluation of the potential deposition of silica, silicates and other scales was done in several stages employing different methods to come up with different sets of data that succeeded one technique after the other. The techniques used are the following: laboratory evaluation (Section 3), geochemical modeling (Section 4), polymerization vessel (Section 5), and side stream rig test (Section 6). As mentioned earlier, pH modification using sulfuric acid was the focus in the first three stages, thus the chemical inhibitor was only tested in the pilot testing stage using an in-house fabricated side stream rig.

The critical parameters that were incorporated in the aforementioned techniques and methods were temperature, pH, and brine residence times. Targeted temperatures were 140-150°C (current brine line conditions), ~100°C (temperature in ORC) and ~60°C (ORC outlet temperature). Target pH was based on initial laboratory results. Residence times of the Marbel brine were five minutes (inside the ORC) and one hour (down to RI well permeable zones). More brine line conditions were included in the side stream rig test (pilot test).

3. LABORATORY EVALUATION

The laboratory evaluation was carried out to estimate the volume of sulfuric acid required to bring Marbel brine from pH ~7 to pH 4.5-5.0. Titration method was employed to determine the buffering zone, where injection is desirable.

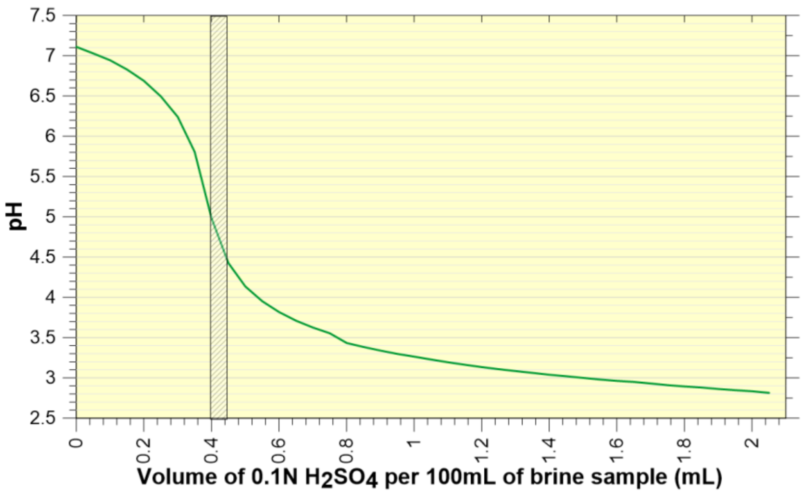

Figure 3. Graph showing MAGP brine titration curve using sulfuric acid.

Steep change in pH unit occurred between pH 5.0 and pH 6.0. This would mean that controlling pH within pH 5.0-6.0 will be difficult, and would require a smaller pump to be less prone to either under-dosing or over-dosing in the pilot test. Hence, with pH target of 4.5-5.0, it was expected that pH would fluctuate at 0.2-0.8 pH unit even with 0.05 mL volume of acid over or under dosage. pH was one of the closely monitored parameters in the pilot test.

4. GEOCHEMICAL MODELING

To further evaluate the chemistry involved in the addition of sulfuric acid in the Marbel brine, saturation indices (in terms of mineral solubility product constant, Log [Q/K] values) of selected minerals were derived using geochemical software. The software that were utilized to identify which minerals (scales) have the potential to precipitate and deposit, under both baseline and binary process conditions, were SOLVEQ-xpt developed by Reed (1982), and WATCH (v2.4), developed by the Iceland Water Group (Arnorsson et al., 1982).

The saturation state of Marbel brine with respect to some common-scale forming minerals was assessed with the aid of the speciation programs SOLVEQ-xpt and WATCH. In general, these programs compute the chemical composition of the geothermal fluids based on the chemical analysis results of water samples collected at the surface. The programs were used to derive and compute the resulting Log (Q/K) values of the selected minerals, when the fluid is cooled (140-150°C to 100°C to 60°C), and is treated with sulfuric acid (from line pH ~7 to 4.5). If Log (Q/K)<0, then the mineral is deemed to be in an undersaturated state. The brine is deemed oversaturated with the mineral if Log (Q/K)>0. Selected scale-forming minerals were anhydrite, calcite, smectite, amorphous silica (am.sil.), pyrite, stibnite and orpiment. All of these were derived from the SOLVEQ-xpt modeling runs, while only anhydrite, am.sil. and pyrite were derived from WATCH (v2.4) due to data input limitations. While the calculated Log (Q/K) values were different from the SOLVEQ-xpt and WATCH programs, the patterns follow similar trends.

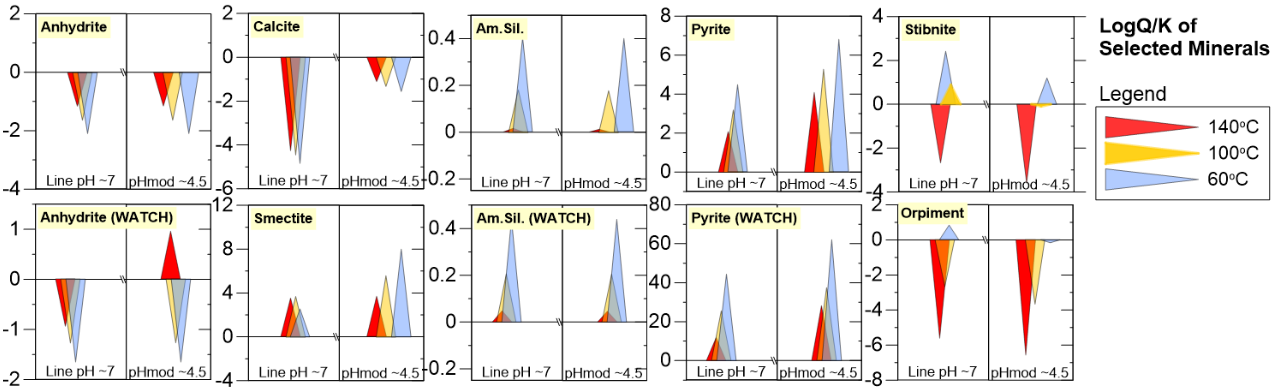

Figure 4. pH (x-axis) vs. Log Q/K (y-axis) graphs derived from SOLVEQ-xpt and WATCH (v2.4). Selected scale-forming minerals were anhydrite, calcite, smectite, amorphous silica (am.sil.), pyrite, stibnite and orpiment. All of Log Q/K values from these minerals we were derived using SOLVEQ-xpt modeling runs, while only anhydrite, am.sil. and pyrite were derived from WATCH (v2.4).

The plots in Figure 4 show the sensitivity of the saturation indices of certain mineral to change in temperature and pH. Brine cooling is the main process involved, and most minerals exhibit prograde solubility. Retrograde minerals such as anhydrite ($CaSO_4$) and calcite ($CaCO_3$) show decreasing Log (Q/K) values in cooler temperatures, and are not expected to form in binary conditions. Most prograde minerals have higher potential to form in lower temperatures. Some of the minerals that have the potential to precipitate if brine temperature is dropped to 60°C and if the pH is modified to 4.5, are smectite, pyrite, stibnite, and amorphous silica (am.sil.). The modeling results also indicate that only orpiment have lower precipitation potential at lower pH. Arsenic sulfide and antimony sulfide (i.e. stibnite and orpiment) are among the major concerns when implementing pH-modification systems in binary plants, and are investigated further in Section 6. Lowering of pH does not really prevent silica to precipitate; rather, it retards silica polymerization and consequently, silica deposition. The results of this modeling exercise were used as a guide to identify elemental components of scales collected after the pilot test (Section 6) via SEM-EDS.

As the primary scale in focus of this study is silica, another geochemical software, SILNUC, was utilized. SILNUC is a modified computer program that was originally introduced by Weres (1980). It can simulate the progression of geothermal brine in terms of monomeric silica, factoring salinity, acidity, and colloid particles. The induction time of silica can be derived from the output of this software. Both of this simulation and the polymerization vessel method (later discussed in Section 5) were conducted to confirm if silica polymerization does not really occur at line temperature (140 - 150°C), to determine the induction period when brine temperature is lowered to ~100°C, and to test the effectiveness of lowering the brine pH in halting silica polymerization beyond its induction period. It is reflected in the simulation results using SILNUC (Figure 5) that lowering the pH of the Marbel brine to 4.5 – 6.0 is effective in prolonging the induction time of silica.

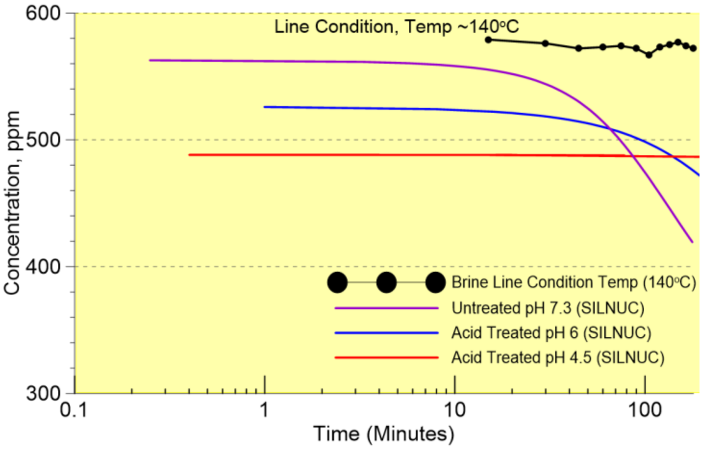

Figure 5. Graph showing simulated silica induction results using the modified computed program. The x-axis is time in minutes, adjusted to logarithmic scale, while the y-axis is concentration in ppm. The black line is at the line conditions. Purple one is at 90°C without treatment. Acid was injection in blue line (pH 6.0) and in red line (pH <6.0), at 90°C.

5. POLYMERIZATION VESSEL METHOD

A polymerization vessel is a pressurized temperature-controlled vessel with inner chamber for water sample retention, which is jacketed by the outer chamber to maintain the desired temperature using excess brine. This method is used to determine the silica induction time at varying temperature and at test pH. The polymerization vessel was inserted along brine lines with flowing brine in the field. The brine was cooled to ~90°C inside the vessel during the field tests. This was the lowest possible degree where stable temperature was achieved.

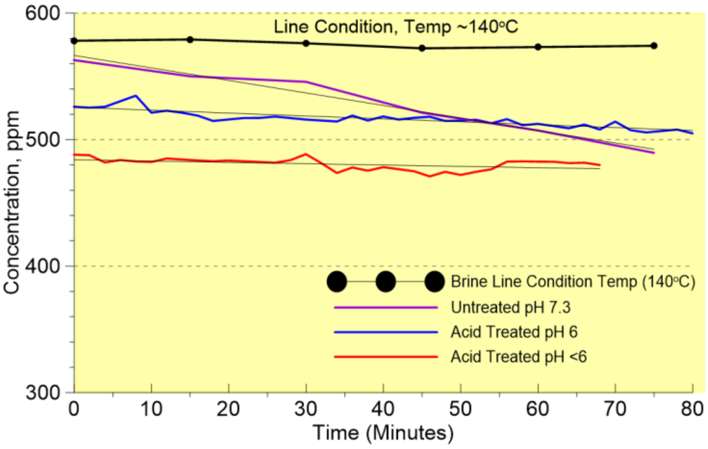

Figure 6. Graph showing field test silica induction results. X-axis is time, while y-axis is concentration. The black line is at line conditions. Purple is at 90°C w/o treatment. Acid was injection in blue (pH 6.0) and in red (pH <6.0), at 90°C.

Silica induction time is important to know because it is the sufficient time to allow the brine to migrate from brine line to heat exchangers and deep into the injection formation before significant polymerization occurs (Gallup, 2011). In the case of the proposed binary plant, it is being investigated if acidification of brine retards the kinetics of amorphous silica polymerization beyond fluid residence in binary plant and down to injection well bore formations. Sulfuric acid was used to adjust pH from 7 to 4.5-6.

Total silica concentration of Marbel brine fluctuates but usually hovers around 580 ppm. This is equivalent to the monomeric silica value at line condition (black line in Figure 6) (140-150°C temperature) which did not drop even after three hours of field test, indicating that silica polymerization does not occur at line conditions. This is also supported by its SSI which is either below or equal to 1.0.

For the second test, untreated Marbel brine was cooled from line temperature of 140-150°C to ~90°C. SSI increased to ~2, which means higher potential for scaling, but may or may not affect the rate of scaling which is dependent on chemical kinetics. Monomeric silica concentration is lower by 24 ppm than the total silica after 15 minutes (purple line in Figure 6). Induction period at ~90°C may be even shorter than 15 minutes.

In the third and fourth tests, the brine was also cooled. At a temperature of ~90°C, SSI is ~2.0. Referring to the blue and red plots in Figure 6, lower pH at both 6.0 and <6.0 evidently does indeed retard silica polymerization, as monomeric silica concentration does not drop much even after lowering brine temperature to ~90°C. Silica inhibition is more effective when pH is lower than 6.0.

6. SIDE STREAM RIG TEST (PILOT FIELD TEST)

The side stream rig test was done to simulate process conditions, to which Marbel brine would be subjected, especially the two-stage brine cooling as it would be utilized to transfer heat to the binary working fluid in the heat exchangers. This field test was conducted to estimate the scaling rates, to identify the mineral deposits, and to determine if there will be other process chemistry issues like corrosion or other scale formation as a side effect of the addition of acid or chemical inhibitor. Three tests were conducted: baseline (no treatment) test, pH-modification test and chemical inhibitor test. A schematic diagram of the pilot test set-up is shown below in Figure 7.

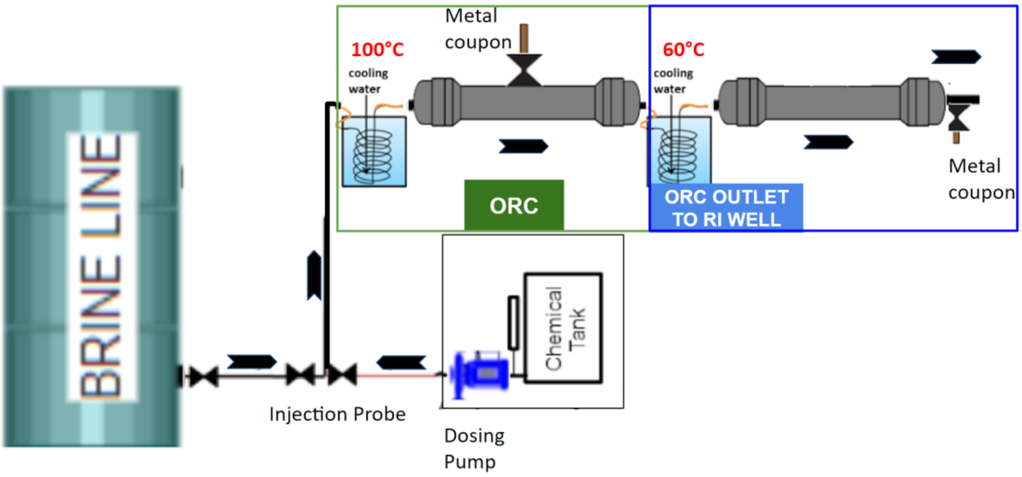

Figure 7. A schematic diagram of the side stream test set-up. Hot brine fluid (150°C) was tapped from the brine line, and diverted to a test rig. The acid or chemical inhibitor was injected before the first cooling stage. The brine was cooled to 100°C and was retained in a vessel for 5 minutes, simulating the ORC plant process conditions. Downstream, temperature was further cooled to 60°C and retained for one hour in another vessel to represent the pipeline and re-injection facilities conditions.

The parameters that were controlled and closely monitored are temperature, pH, chemical injection rate, brine flow rate and line pressure. Visible scaling along the rig line, and monomeric silica concentration were also monitored regularly. Metal coupons were inserted at key sections for post-test analysis of deposits, and determination of weight gain or loss. Water chemistry data and petrographic data were obtained from brine samples and scale samples, respectively.

6.1 Silica Trends

As shown in the graphs in Figure 8, a slight decrease in monomeric silica ($mSiO_2$) occurred after brine cooling to 100°C in all tests except in the pH-modification (pH-mod) line. Further cooling to 60°C, $mSiO_2$ dropped even more in both the untreated line and the inhibitor-treated line, showing the ineffectiveness of the chemical inhibitor to inhibit silica polymerization at these conditions. Meanwhile, the pH-modification (pH-mod) (average pH of 4.7) method shows good results in retarding silica polymerization, as the total silica clusters coincide with the monomeric silica clusters in both sampling points.

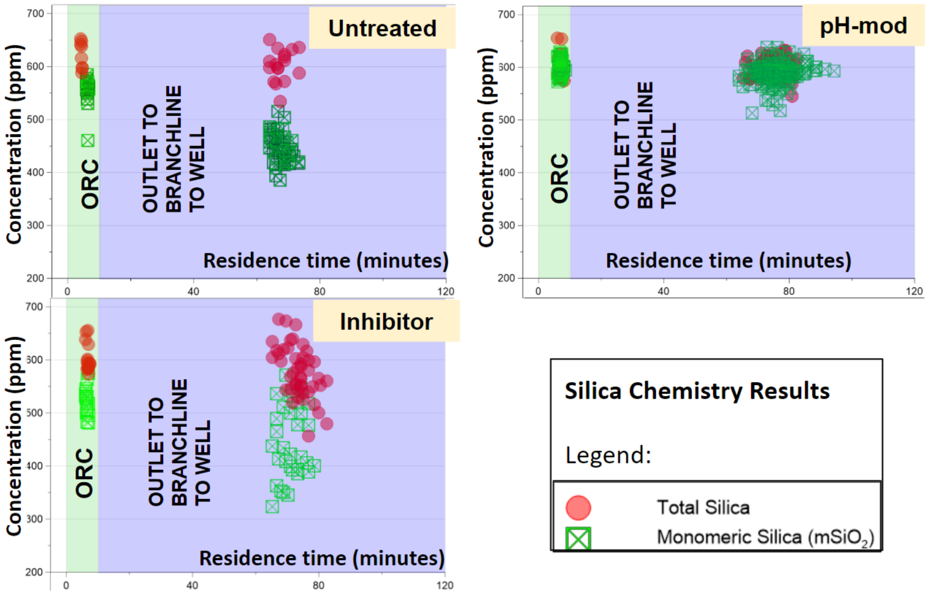

Figure 8. Silica concentrations that were clustered based on sampling points (100°C - 1st sampling point, and 60°C - 2nd sampling point).

6.2 Post-Test Inspection

Inspection of the 100°C vessel showed different degrees of silica deposition for each of the three tests, from pH-mod, untreated (baseline), chemical inhibitor in order of smaller to greater amount of deposits. White powdery fine-grained deposits were found in the 100°C vessel in all lines except in pH-mod.

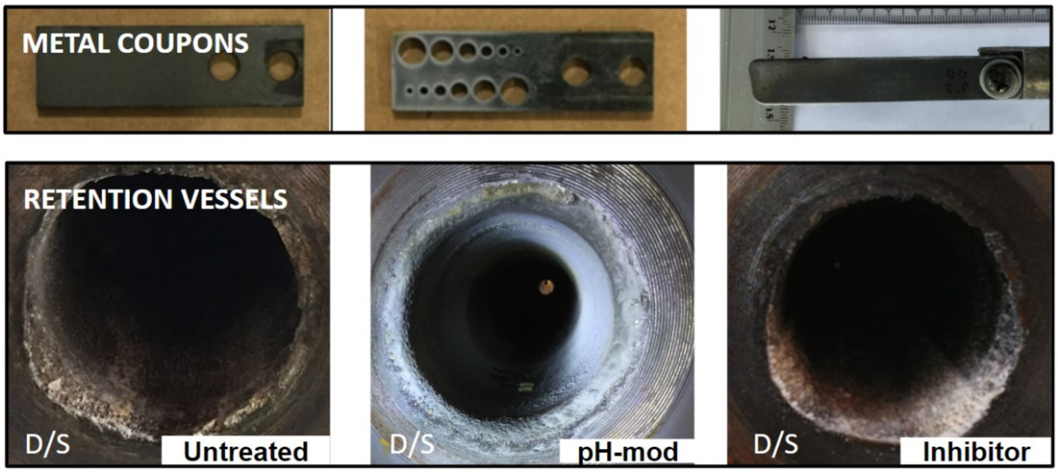

Figure 9. Metal coupons were inserted in the 100°C vessel representing the ORC plant, for estimation of scaling rate of collection of scale samples viable for SEM-EDS analysis.

For the metal coupons, the most apparent observation is discoloration. Coupons from the chemical inhibitor test show deposition of gritty, white to greenish brown materials. More in-depth analysis of the scales was done through thin section method (using petrographic microscope) and/or SEM-EDS (scanning electron microscopy-energy dispersive x-ray spectroscopy) analysis.

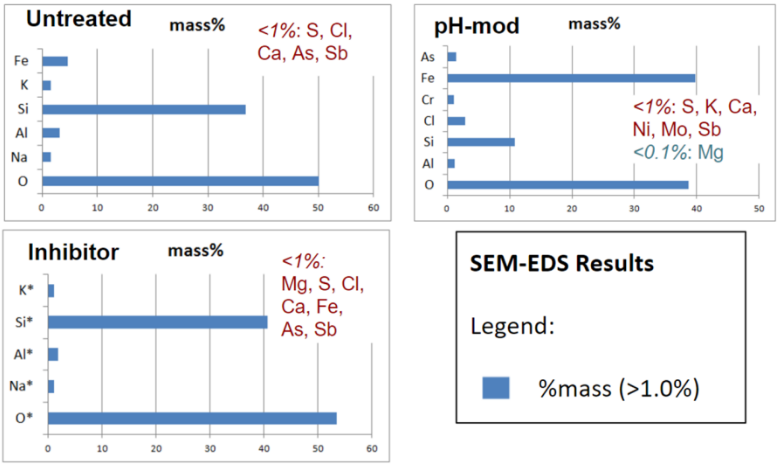

Figure 10. SEM-EDS results of the metal coupons from RV1 (represents ORC plant).

SEM-EDS analysis was done only on metal coupon samples. Scales collected from the pipes could not be mounted on the stage of the SEM as it could damage the instrument due to scale samples' incohesive and powder-like form.

Most common chemical components found in the metal coupon samples are Si and O that compose silica (SiO_2). Other components detected were Fe, K, Al, Na, and Ca that are of significant amount in both Untreated and pH-mod lines, consistent with the results of geochemical modeling and thin section analysis results. One of the risks in binary plants in geothermal fields is the precipitation of antimony (Sb_2S_3) and orpiment (As_2S_3), especially where pH-mod is being utilized. Small amounts of Sb, As and S are present in the metal coupon samples in both untreated and pH-mod tests.

Below is a table (Table 1) showing deposition and corrosion rates based on initial and final weights of the inserted coupons in the 100°C vessel. The unit is in millimeters per year (mmpy).

Table 1. Calculated deposition and/or corrosion rates for the ORC segment.

100°C Vessel	Untreated	pH-mod	Chemical inhibitor
Deposition/ Corrosion Rate	0.123mmpy	-0.0247 mmpy	1.15 mmpy

The chemical inhibitor line exhibited faster silica (predominant based on SEM-EDS results) deposition rates with over 1 mmpy than the untreated line 0.123 mmpy at 100°C temperature, which implies ineffectiveness of the chemicals to inhibit silica scaling. The mass of the metal coupon in the pH-mod decreased as expected due to lowering of pH from 7.4 to 4.5, although the corrosion rate of -0.0247 mmpy is still tolerable.

Mineral scaling is more prominent in this segment of the test rig than in the ORC segment. Post-test investigation of the 60°C vessel showed different degrees and forms mineral deposition for each of the five tests. Photographs of the formation vessels and metal coupons are shown below in Figure 11.

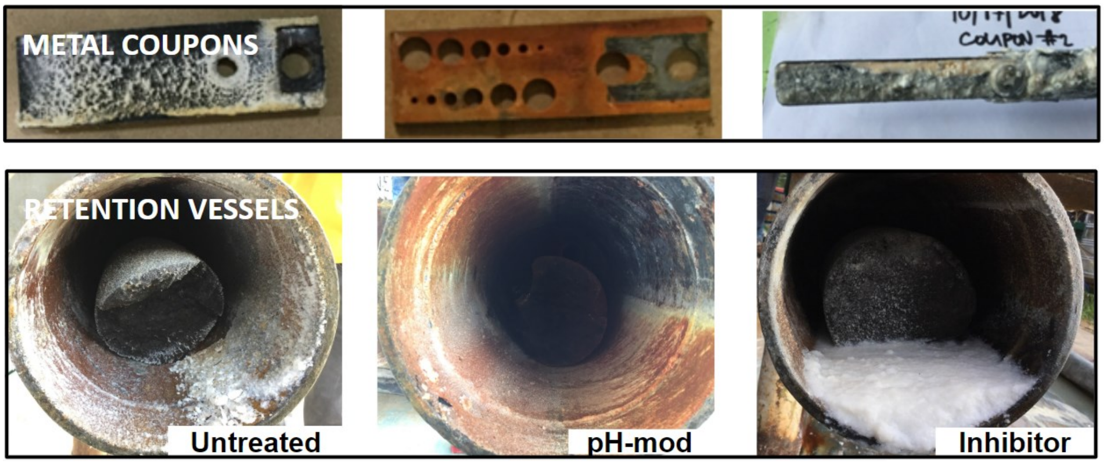

Figure 11. Metal coupons were inserted in the 2nd retention vessel (RV2) representing downstream of the binary plant down to the re-injection wells (RIW), for estimation of scaling rate of collection of scale samples viable for SEM-EDS analysis.

In the Untreated (baseline) test, soft, flaky white-brown scales are deposited on top of hard, white vitreous scales. It can be inferred from this that amorphous silica deposited through colloidal formation and direct deposition. This can be supported by thin section analysis results. No SEM-EDS data are available for the untreated line due to insufficient amount of samples after thin section analysis. For the pH-mod line, a very thin layer of soft, orange-tinged deposits were found on the inner pipe surface. SEM-EDS analysis reveals the major components are Fe, Si, O, Sb, and S. Iron oxides, silica and stibnite may be the primary scales in the pH-mod line percentage-wise, but are only present in microscopic amounts.

Based on SEM-EDS data, silica scales also compose most of the deposits in the inhibitor-treated lines.

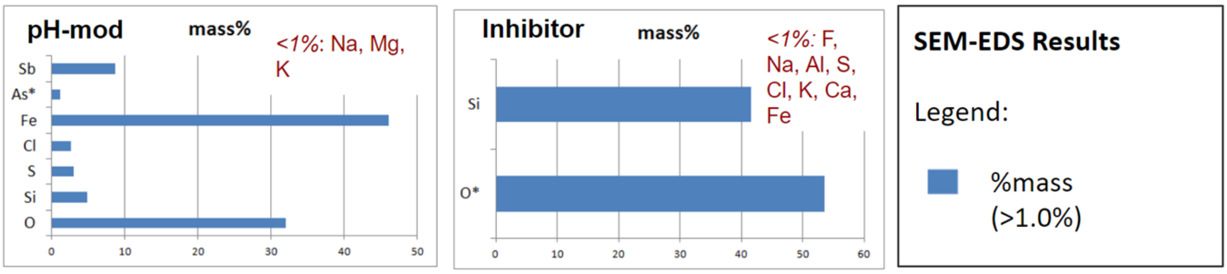

Figure 12. SEM-EDS results of the metal coupons from RV2 (represents downstream of ORC). Note: No SEM-EDS data are available for the untreated line due to insufficient amount of samples after thin section analysis.

Deposition/corrosion rates were derived from metal coupon weight loss or gain. These are shown in Table 2.

Table 2. Calculated deposition and/or corrosion rates for the portion representing downstream of ORC.

60°C Vessel	Untreated	pH-mod	Chemical inhibitor
Deposition/ Corrosion Rate	0.827mmpy	-0.067 mmpy	8.70 mmpy

Table 2 data show that in the untreated line, scaling rate increased in the 60°-vessel where temperature was cooled to 60°C. This was also observed in the inhibitor-treated line, showing again the ineffectiveness of this chemical to inhibit silica scaling at these conditions. Weight loss was derived from the pH-mod line implying corrosion was more prevalent than mineral scaling, but the presence of scales in the metal coupons was only detected through the SEM equipment (SEM-EDS). Higher corrosion rate was observed in the 60°C portion than in the 100°C, which was not expected. This can be attributed to greater degree of flow turbulence in the 60°C, as the metal coupon was inserted in an elbow section.

7. CONCLUSION

In the first three methods (laboratory evaluation, geochemical modeling, and polymerization test), sulfuric acid was the only chemical used, while both sulfuric acid and a chemical inhibitor was used in the side stream rig test (pilot test). Based on the titration curve produced by laboratory evaluation, the optimal pH range that should be targeted was 4.5 to 5.0. The polymerization test aimed for this pH range. The results showed that silica polymerization can be delayed when pH is dropped to ≤6.0 at 90°C temperature; while monomeric silica dropped faster in the untreated brine at the same temperature. Geochemical modeling results using SOLVEQ-xpt and WATCH also identifies potential precipitation of amorphous silica if no treatment is done upon cooling of brine to 100°C and 60°C, but suggests potential scaling of stibnite and clay. This was validated in the side steam test rig, where chemical treatment trials were conducted, but only amorphous silica poses massive scaling issue. The inhibitor chemicals failed to prevent silica scaling, and only the pH-modification (pH-mod) process using sulfuric acid provided desirable results to minimize (and possibly prevent) silica fouling.

Field test results showed that pH-mod (lowering of pH from ~7.3 to 4.7 via acid-dosing) is the most effective method in solving the silica problem for the Mt. Apo binary project. The silica trends are consistent with the visual inspection and petrographic results, indicating that pH-modification is an effective solution to retard formation and deposition of amorphous silica inside and further downstream of the binary plant. However, since corrosion risk accompanies the pH-mod method, a robust pH monitoring with automatic response between pH and brine flow rate is critical to the operability and seamless operations of the silica inhibitions system. Corrosion probes and metal coupons will be inserted within the brine line to monitor scaling and corrosion rates. There are already existing and working facilities that demonstrate the treatment effectiveness of pH-mod system in geothermal binary plants, such as in Puna (Hawaii) and Ngatamariki (New Zealand).

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