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Simultaneous Silica Treatment Qualification Using On-Site Side Stream Test Rig

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ABSTRACT

An on-site side stream test program has been developed to thoroughly assess the required mitigation for silica scaling of a proposed brine optimization project in Bacon Manito (BacMan), Sorsogon, Philippines. The test rig simulated the temperature drops, residence time, and flow regime of the brine-optimization-plant-to-reinjection system. A base-case test line and treatment lines with dosing provision were simultaneously operated for ~30 days, alongside a field laboratory for immediate silica analysis. Out of four different chemical treatments, the most effective silica inhibition method was evaluated based on silica retention performance, and volume of actual scale deposits formed. Brine pH modification proves to be the most efficient silica scaling mitigation method for the project area, resulting to manageable scaling rates.

1. INTRODUCTION

In the pursuit to further generate power from its current operational setup, EDC has resourcefully identified projects like brine optimization as a resource strategy. Before reinjection, further heat extraction of the separated brine stream from existing BacMan Unit 1 power plant is possible through Binary Organic Rankine Cycle (ORC) technology.

The proposed binary plant use heat exchange to exploit geothermal fluid to heat up and vaporize a secondary fluid driving a turbine producing electric power. The heat exchange cools down the 170°C brine to a temperature of about 80°C which consequently increases the Silica Saturation Index (SSI) of BacMan brine from ~1 to 2.5-3.0. The higher SSI means higher potential for silica deposition. Silica deposition reduces the overall efficiency of the heat exchangers, introduces the risk of blockage in the reinjection pipelines and wells, and lowers the permeability in the subsurface formation as silica deposits.

Understanding and resolving the silica deposition risk that comes with heat extraction from the brine is a proactive approach in dealing potential problems of the binary plant operation. Implementing a pilot test rig to simulate the binary-plant-to-reinjection system with the opportunity to test different chemical treatments helped provide a more informed strategy in fighting the silica scaling problem and plan for subsequent risks.

This paper discusses the process and design employed by EDC to evaluate the optimization strategy, identify the best-suit silica mitigation approach for the Palayan Bayan brine in BacMan, and the issues encountered and rectified.

2. METHODOLOGY

The initial test rig design did not result to any silica scaling despite rapidly cooling the brine from~170°C (line temperature) to ~80°C (target plant outlet temperature). Series of induction time tests were immediately conducted to fully understand the scaling potential. The team then decided to modify the test rig after further review of the brine induction time and residence time. The test rig re-design considered the kinetics of silica deposition of the BacMan brine, and provided a complete system representation from tapping point, to the binary plant, then the reinjection lines and finally to the reservoir (Figure 1).

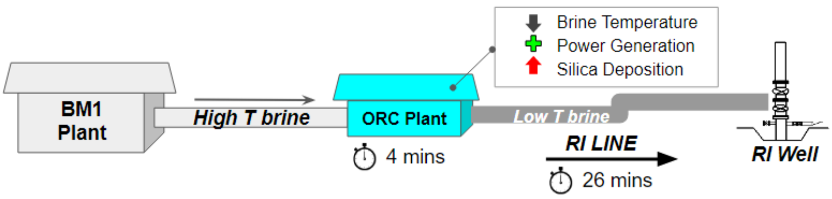

Figure 1: Schematic diagram of plant-to-reinjection system.

2.1 Silica profiling

Silica deposition is mainly controlled by thermodynamics and kinetics, the former allows the prediction of what is expected to happen when equilibrium is reached and the latter is responsible for how fast this equilibrium is achieved (Brown, 2011). In most geothermal surface facilities, amorphous silica is precipitated as an effect of bringing hot geothermal waters to the surface. This is due to the difference in silica solubility – when hot water is underground, it is in equilibrium with quartz then it goes through a considerable drop in temperature as it is extracted to the surface, and aqueous silica levels are then controlled by equilibrium with amorphous silica. This equilibrium is conveniently expressed in terms of Silica Saturation Index or SSI (Barnett and Garcia, 1993). A resulting SSI value of >1.0 indicates the brine is supersaturated and thermodynamically must eventually deposit amorphous silica:

$$SSI\ (T) = \frac{total\ SiO2\ aq}{(Solubility\ amorphous\ silica)at\ T}$$

Silica content of the BacMan brine averages at 712 ppm at the reinjection line tapping point (~170°C). At this location, the silica saturation index (SSI) is <1.0. Further cooling of the brine results to increasing SSI (Figure 2). At around 140°C, the SSI of the brine starts to exceed 1.2 (EDC operational SSI limit), and further increases to ~2.2-2.6 at 80°C. These data suggest silica oversaturation at the exit point of the brine plant, signifying that deposition is likely expected. Therefore a robust mitigation plan must be in place; this begins with identifying how fast it takes before silica polymerization and deposition start to happen.

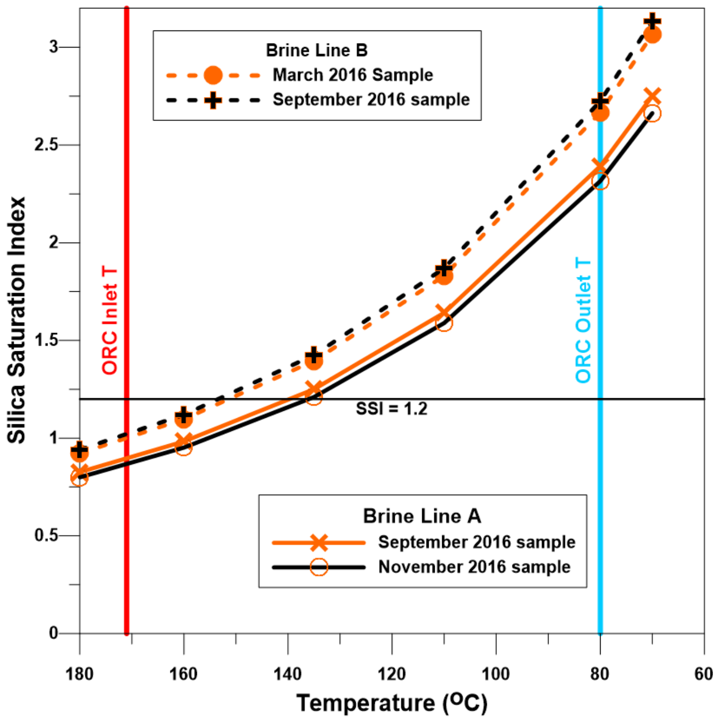

Figure 2. SSI profile of BacMan brine at different temperatures

Another factor in the kinetics of silica deposition is the presence of other ions in solution. Positive ions such as Na^+ reduces electrostatic repulsion leading to rapid agglomeration, consequently rapid scaling, while the presence of highly charged ions like Al^{3+} and Fe^{3+} bridges colloidal agglomeration (Brown, 2011). Palayan brine is highly saline with minimal presence of Fe, Mg, Sb, and Al. Table 1 shows the concentration of some ions sampled at the inlet of the test.

Table 1. Selected ion concentrations in Palayan brine.

	In mg/kg									
pH (Temp)	**Na**	**K**	**Ca**	**Mg**	**Fe**	**Cl**	**SO_4**	**SiO_2**	**Sb**	**As**	**Al**
6.5 (21.7)	5270	949	267	0.22	0.1	9715	23	627	0.138	5.64	0.090

2.1.1 Induction Time Tests

Using a silica polymerization vessel and following the standard EDC procedure (Alcober et al., 2005), series of induction time tests were conducted – starting off with the uncooled, untreated Palayan Brine and the cooled to 80 °C condition. Figure 3 shows the results where it is apparent that at line conditions, the silica shows minimal polymerization, whereas cooling the brine down to 80°C has a massive effect on the polymerization of silica with the induction time almost instantaneous. Significant polymerization of silica is seen after 20 minutes where a drop of ~100 ppm monomeric silica is observed. This also suggests unlikelihood of silica deposition within the ORC block (~4 minutes brine residence time), but is expected otherwise in the reinjection lines and borehole (>10 minutes).

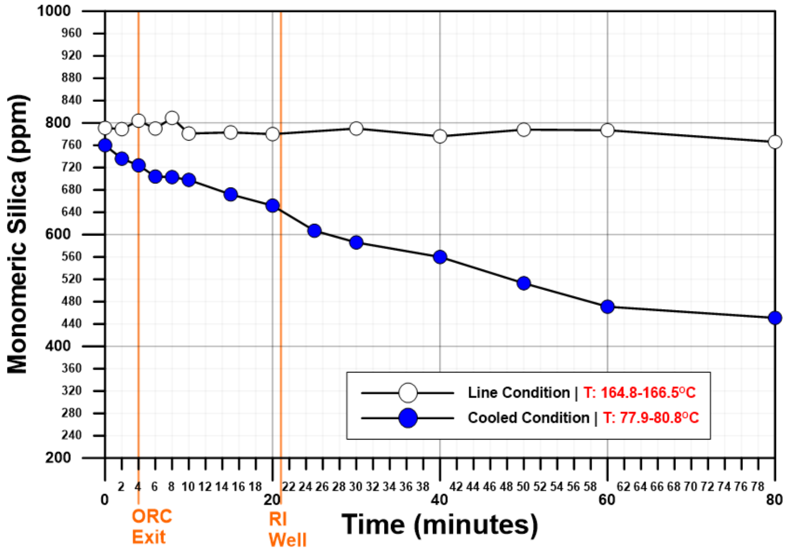

Figure 3. Silica induction time tests at line condition and at cooled condition

Induction time tests with treatment using various inhibitors documented the difference on silica polymerization profiles. Figure 4 shows how silica polymerization in inhibitor-treated brine is closely within the silica profile of the untreated brine. Based on the monomeric silica trends, all the inhibitors do not prevent polymerization within the RI residence time. At this point, the treatment that best delayed silica polymerization was pH modification using sulfuric acid. It was also noted that monomeric silica concentration declined after the 60-minute mark of the acid-treated line plot.

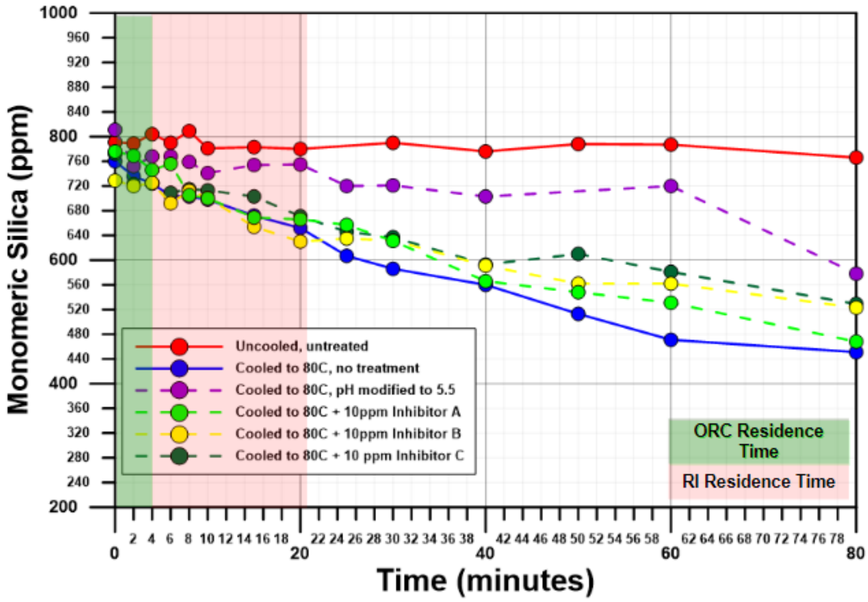

Figure 4. Silica induction time tests of different chemicals

The induction time tests gave an outlook on how different treatments were expected to perform but the side stream testing will ultimately simulate the actual binary set-up until reinjection and provide data at extended exposures that can strengthen or nullify these initial findings.

2.2 Treatment options

For this test, pH modification and the use of chemical inhibitors were the treatments considered. Both target the formation or coagulation of colloidal silica to retard deposition. pH modification was done by injecting dilute H_2SO_4 to bring down the pH from ~7 to 4.5-5.0, the usual target pH in some successful plants, e.g. Puna and Rotokawa (Table 2). The dosing concentration was identified from laboratory titration of sulfuric acid to the BacMan brine.

Four different chemical inhibitors from various suppliers were tested at similar concentration, 10 ppm. Chemical inhibitors change the surface characteristics of the colloid such that the energy barrier to approach another colloid is increased. They function as dispersants for the colloidal mechanism of silica.

Table 2. Known binary power plants in operation using pH modification

Plant	SSI	Capacity, MWe	Year Commissioned	Target pH
Puna, Hawaii	**4.0**	8	2012	4.5
Sarulla	**3.0**	30	2017	4.5-5.5
Blundell, Utah	**2.4**	12	2007	
Rotokawa, NZ	**1.4**	34	1997	5

2.3 Side stream test rig

2.3.1. Binary-to-reinjection-system analog

Actual brine from the source plant was tapped to ensure similar brine characteristics. Main components of the ORC plant were provided for in the design in the same order and flow conditions. Heat exchangers which conductively cool the brine, gradually from 170°C to 80°C was replicated by installing a series of cooling systems composed of coiled tubings. This was in tandem with a steady supply of cooling water to achieve the temperature drops within the binary plant. Mini-thermowell assemblies were placed in between each cooling system to monitor the target temperatures (Figure 5). Other critical parameters such as flow velocity and Reynold's number were maintained within the ORC block analog of the setup for dynamic similitude.

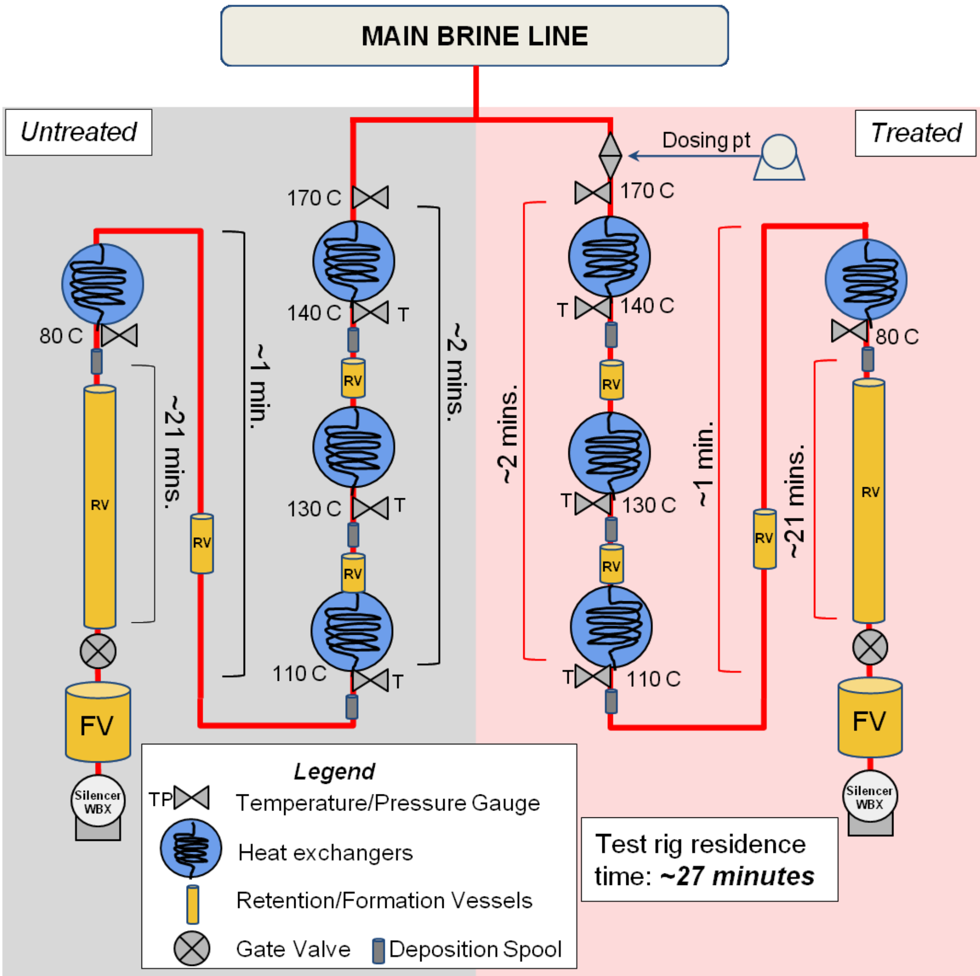

Figure 5. Schematic diagram of the simultaneous silica treatment test rig

The reinjection pipelines were represented by carbon steel pipes after the "ORC block". Retention vessels were added to the test rig to extend the brine residence time similar to how long it will take for BacMan brine to reach the reinjection wells. Change in velocity and flowrate within these vessels causes a laminar flow to the brine, which is prevented by installing baffles inducing static mixing and a turbulent flow. The test pipelines and retention vessels were insulated to minimize temperature drops. Then, a last vessel containing cut-up cores of formation materials is incorporated to represent the water-rock interaction at the reservoir. Note though that temperature and pressure were not simulated in this section of the rig, and this segment was particularly repeated through a third party laboratory that has the capacity to replicate the water-rock interaction and T, P conditions.

A dosing point is located after the inlet sampling point of the test line to allow for treatments testing. Dosing consistency is controlled by a pump with calibration column. For the pH modification test run, an online pH monitoring system was installed.

2.4 Data collection and analysis

To ensure that the target ORC parameters are replicated throughout the test, monitoring instruments were placed at strategic locations. Pressure gauges were installed at the inlet and the outlet to check if line pressure is constant. As mentioned above, mini-thermowell assemblies are placed in every cooling system. Isolation valves are placed at the outlet to control flowrate and keep it at 0.20 kg/s target. The flowrate is measured through a mini silencer weirbox at the end of each test line. While monitoring of pH along the acid-treated test line was through the use of an online pH meter taking readings at real time.

To comprehensively document scaling within the system, deposition spools were installed after every cooling system and were pre-weighed before the start of the test. Scale thicknesses were measured using a caliper, and then converted to volume. Scale characterization was through petrographic and SEM analysis.

A baseline run without any treatment was conducted for reference. Water samples were gathered regularly, to monitor silica content – monomeric and total. The immediate analyses of monomeric silica from these samples were performed using a portable ultraviolet and visible (UV-Vis) absorption spectroscopy instrument. Then simultaneous treatment runs, maximum of two lines at a time, were carried out and documented.

3. SIDE STREAM TEST RESULTS

The key performance metrics for the side stream test are: silica retention in brine based on chemistry and least scale buildup based on volume. For fair evaluation, physical parameters such as flowrate, dosing rate, line pressure were achieved and maintained at the start of every test run and were monitored for any changes indicating major or total blockage.

The test runs mostly completed the 30-day trial, except for inhibitor B which clogged up the test line after just 7 days, (Figures 6-7). The chemical composition of the inhibitor is undisclosed but upon discussion, it was discovered that the formulation has deficiencies at SSI levels beyond 2.2. Recall that BacMan brine is around 2.5 at the outlet test condition. This automatically removes Inhibitor B from the mitigation options considered. See subsections below for more discussion of the results.

3.1 Silica retention performance

A straightforward approach for comparative analysis of treatment performance in the brine is observed with the total silica versus monomeric silica concentration plot through time (Figure 6). The average total silica content in Palayan brine is represented by the blue horizontal line. Ideally, the best treatment would have to have a monomeric silica plot very close to this reference line, indicating least polymerization. The trendlines confirm the initial induction test results wherein pH modification is the most successful as silica remained dissolved in solution, and theoretically should lead to least silica deposition. It has outperformed the polymer inhibitors which plotted trendlines below the reference line, and are also trending slightly downwards towards the end of testing. As expected, the untreated, cooled brine generally plotted the lowest from the total silica line.

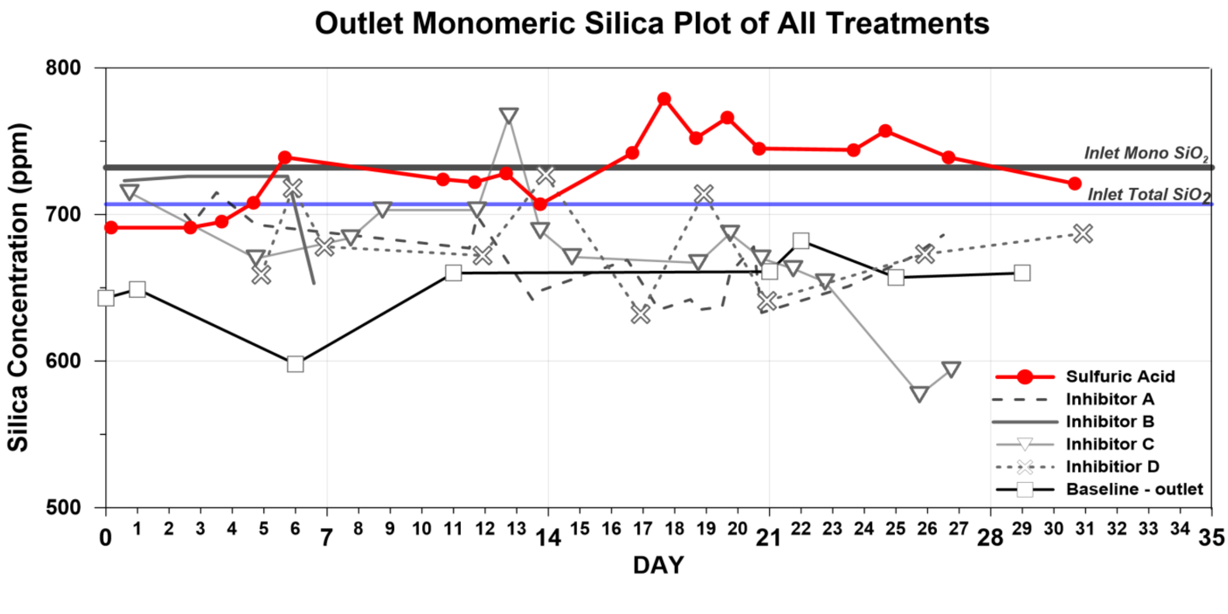

Figure 6. Silica trend lines per test run versus reference total silica concentration of the brine at the inlet

3.2 Visual inspection and weight difference

Table 3 summarizes the increase in weight of the deposition spools and formation vessel, and the thickness of scale deposits on the retention vessels at the end of 30-day testing. The least measured deposits are highlighted. Within the ORC plant analog, it appears that leaving the brine untreated is the best strategy to retard any deposition leading to blockage. But upon exiting the plant at a temperature of ~80°C, the acid-treated brine shows least deposits formed as evidenced by weight percentage increase.

Table 3. Summary of measured deposit and percentage increase per test run

Analog	Location	Baseline		Inhibitor A		Inhibitor B*		Inhibitor C		Inhibitor D		Sulfuric Acid (pH ~4.8)	
		MD	% Inc	MD	% Inc	MD	% Inc	MD	% Inc	MD	% Inc	MD	% Inc
ORC Plant	Deposition Spool (1) at T~140°C (g)	1.00	**0.28**	2.00	**0.53**	0.00	**0.00**	1.00	**0.52**	2.40	**0.67**	7.00	**2.34**
	Deposition Spool (2) at T~130°C (g)	0.00	**0.00**	0.00	**0.00**	0.00	**0.00**	3.00	**0.83**	1.10	**0.33**	4.00	**1.13**
	Deposition Spool (3) at T~110°C (g)	0.00	**0.00**	3.00	**0.82**	5.90	**1.59**	3.00	**0.74**	0.00	**0.00**	2.00	**1.07**
	Deposition Spool (4) at T~80°C (g)	3.00	**0.68**	1.00	**0.28**	1.00	**0.27**	6.00	**1.70**	1.70	**0.86**	2.00	**0.69**
RI pipeline	Retention Vessel w/ baffles (in)	0.54	-	-	-	-	-	-	-	-	-	**0.02**	-
Reservoir	Formation Materials (g)	483.00	**4.39**	743.0	**3.78**	12841.00	**98.77**	1326.00	**10.54**	389.00	**3.24**	208.00	**1.73**

**7 days accumulation only; MD = Measured Deposit (in grams for deposition spools, in inches for retention vessels); % Inc = Percentage increase in weight*

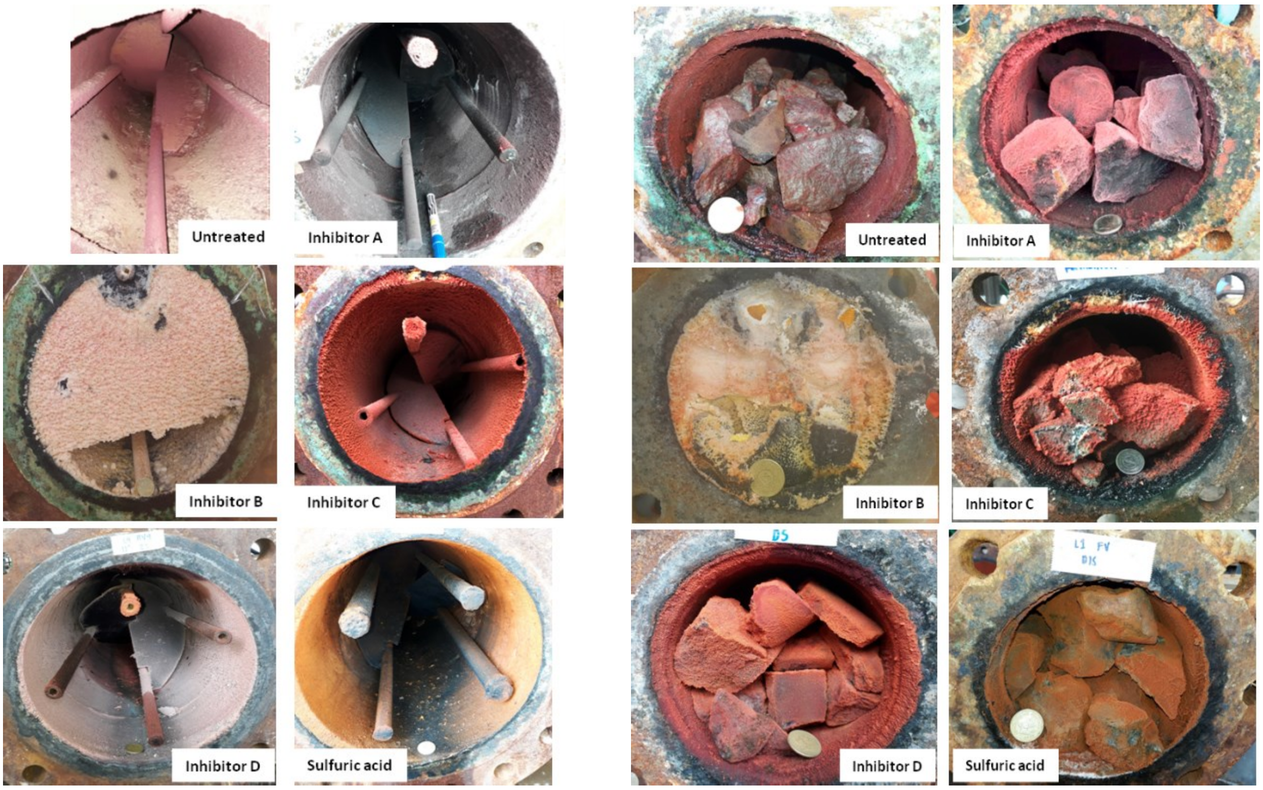

Figure 7. Resulting scale deposits on the retention vessels (left group) and formation vessels (right group) per test run

Visually, least deposits were observed for the untreated, Inhibitor A, and sulfuric acid test runs both in the reinjection pipelines analog (Figure 7, left) and the reservoir analog (Figure 7, right). Ultimately, the treatment that was considered most efficient was still pH modification due to the chemistry results discussed in the previous subsection.

3.3 Scale Deposits Characterization

Scale samples were scraped off from the retention vessel, formation materials and submitted for petrographic and x-ray diffraction analyses for detailed characterization. Meanwhile, the deposition spools within the ORC block were cut in half and sent for scanning electron microscope – energy dispersive x-ray spectroscopy (SEM-EDX) analyses. Table 4 only shows results from the untreated and acid-treated test lines:

For the acid-treated line, the reddish deposits observed covering the internal diameter of the deposition spools, representing the heat exchangers were antimony, sulfur and arsenic in elemental composition. Whether they exist as sulfides or oxides, this cannot be fully ascertained due to absence of XRD analyses. However, this is an indication of amorphous stibnite and/or arsenic sulfide deposits as an effect of lowering the brine pH (Brown, 2013). This has been acknowledged by EDC.

Table 4. Summary of scale deposits characterization through thin section petrographic analyses, x-ray diffraction and scanning electron microscope - energy dispersive x-ray spectroscopy

Test Line	Analog	Microscopic	XRD	SEM-EDX*
Untreated Test Line	Heat Exchanger			Oxygen (43%) Antimony (34%) Silicon (15%) Iron (3%) Sulfur (2%) Nickel (1%)
	RI Pipeline	Amorphous silica (~65%) Amorphous material (~30%) Corrosion products (~5%)		
	Reservoir	Colorless silica (~90%) Hematite corrosion products (~10%)	Amorphous silica	
Acid-treated Test Line	Heat Exchanger			Antimony (46%) Sulfur (33%) Arsenic (10%) Carbon (6%) Iron (2%) Oxygen (2%) Nickel (1%)
	RI Pipeline	Amorphous silica (~55%) Amorphous material (~40%) Corrosion products (~5%)	Amorphous silica	
	Reservoir	Amorphous silica (~200 µm thick) Thin opaque layer (~20 µm thick)	Tridymite, opal, cristobalite (silica polymorphs) Amorphous silica and sulfides	

**Semi-quantitative analysis*

3.4 Scaling Rates

To compute for a linear scaling rate, the weights in volume within the deposition spools were translated into thickness of deposits over the duration of testing. This was calculated by assuming a uniform spread of volume over the length of the pipe. A step-by-step calculation is shown here:

$$V_{measured\ scale} = \Delta W_{as-measured} * \rho_{Amorphous\ Silica}$$

$$Volumetric\ Scaling\ Rate - Test = \frac{V_{measured\ scale}}{\tau_{Test\ Duration}}$$

$$SA_{Test\ Spool} = 2\,\pi \frac{\Phi_{Spool}}{2} * Length_S$$

$$Linear\ scaling\ rate - test = \frac{Volumetric\ Scaling\ Rate - test}{SA_{Test\ Spool}}$$

Where $\Delta W_{as-measured} = scale\ measurement\ in\ weight$, $\rho_{Amorphous\ Silica} = 2.65\ g/cm^3$, $\tau_{Test\ Duration} = test\ days$ $SA_{Test\ Spool} = Surface\ area\ of\ deposition\ spool$, $\Phi_{Spool} = diameter\ of\ deposition\ spool$ and $Length_S = spool\ length.$

Meanwhile for the reinjection line scaling rate calculation, the deposit thickness was first converted to volume to translate the scaling rate to a full flow along the actual diameter of the reinjection pipeline and its actual length from exit point of binary plant to reinjection pad. This was then converted back to linear scaling rate to achieve the resulting value in Table 5.

$$V_{measured\ scale} = V_{Clear\ Hole} - V_{Scaled\ Hole}$$

$$V_{measured\ scale} = \left[\pi * Length_{Spool} * \left(\frac{\Phi_{Spool}}{2}\right)^2\right] - \left[\pi * Length_{Spool} * \left(\frac{\Phi_{Spool} - 2 * \text{Scale Thickness}_{as-measured}}{2}\right)^2\right]$$

$$Volumetric\ Scaling\ Rate - Test = \frac{V_{measured\ scale}}{\tau_{Test\ Duration}}$$

$$Volumetric\ scaling\ rate - full\ flow = \frac{Actual\ full\ flow}{Test\ flow} * (Volumteric\ scaling\ rate - test)$$

$$SA_{Actual\ Reinjection\ Lines} = 2\,\pi \frac{\Phi_{Actual\ Reinjection\ Line}}{2} * Length_{Actial\ RI\ lines}$$

$$Linear\ scaling\ rate - full\ flow = \frac{Volumetric\ Scaling\ Rate - full\ flow}{SA_{Actual\ RI\ lines}}$$

Where $SA_{Actual\ Reinjection\ Lines}$ is the surface area of the actual reinjection pipelines, and $\Phi_{Actual\ Reinjection\ Line}$ represents the diameter.

The calculated scaling rates are as follows, in millimeters per year (mm/year):

Table 5. Scaling rates of untreated versus acid-treated line

Section	No Treatment	With Treatment (pH Target 4.80)
Heat Exchanger 1	0.35	2.46
Heat Exchanger 2	0	1.41
Heat Exchanger 3	0	0.71
Heat Exchanger 4	1.06	0.71
Reinjection Line	14.32	0.56

The scaling rates just reinforce the observation that leaving the brine untreated within the ORC block seems a better strategy than placing a dosing point for pH modification at the inlet. At worst case, a 2.46 mm/year scaling rate is expected at the first heat exchanger upon acid dosing, but decreases in the reinjection lines at a rate of 0.56 mm/year.

3.5 Issues

The implementation of the test rig was not perfect and a lot of issues were encountered before the team successfully commissioned its operation. Listed below are some of the major issues which were eventually resolved in the BacMan setup and were rectified in the next test locations.

1. Solids from brine due to an initial bottom tapping point caused test interruptions
2. Absence of data points within the ORC block analog
3. Leaks during pH modification test due to corrosion at the dosing point
4. Amount of formation materials was not consistent for the test runs
5. The concentration of line inlet monomeric silica is greater than the inlet total silica – an artifact of possibly:
    a. Silica deposition upstream before the tapping point or
    b. Instrument error for monomeric silica analysis
6. Weight or thickness of resulting deposits does not factor in corrosion

4. CONCLUSIONS AND IMPLICATION TO THE PROJECT

Based on the results of the simultaneous silica treatment tests conducted in BacMan, it was proven that the silica scaling problem of the proposed brine optimization plant can be controlled with proper treatment and extensive control and monitoring system. Silica inhibitors function as dispersing agents, while pH modification remains to be the most effective method in retarding silica deposition, This is evidenced by the high retention of silica - for at least 30 minutes – according to the test rig residence time, and at most 60 minutes – according to the polymerization tests. This extension of induction time allows EDC to strategize the brine reinjection system before deposition is expected.

The simultaneous side stream test rig also led to the discovery that injecting downstream the ORC plant might be a better strategy during operations, leaving the heat exchangers untreated. This also influenced EDC on strategizing backup plans, in terms of dosing point locations, if these results do not hold true in actuality.

Another valuable information gathered from this test are the scaling rates that allowed the team to make projections on work-over and pipeline cleaning schedules. A scaling rate of 1.06 mm/year (at worst) and 0.56 mm/year is expected within the heat exchangers and along the reinjection pipelines, respectively if the abovementioned operational strategy is followed. These rates are deemed manageable operation-wise. Meanwhile, the reinjection effects to the reservoir of the cold, acid-treated brine were further evaluated on a separate laboratory testing facility simulating high temperature and pressure conditions.

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