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Characterization of Binary Plant Heat Exchanger Scale Deposits Under Different Treatment Conditions

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ABSTRACT

Mineral scaling insights in a geothermal binary plant can be from geochemical simulation, sidestream testing and actual plant operations. The information gathered from these studies can help provide a clearer picture of the scale deposition behavior. This study investigates the characteristics of scale deposits formed under different binary plant treatment conditions. The conditions considered were untreated, treated with polymer-based inhibitor and treated with pH modification. The collected scale samples were analyzed using x-ray fluorescence (XRF), gravimetry, scanning electron microscopy (SEM) and x-ray diffraction (XRD) to determine their mineralogical composition, morphology and elemental content. From the results, the scales treated with polymer-based inhibitor exhibited a relatively consistent composition of amorphous silica (majority at more than 90% w/w). Untreated and treated with pH modification conditions showed combination of amorphous silica, metal silicates and metal sulfides. Aside from quantitative results, qualitative observations showed that the deposited scales also differ on the physical characteristics like hardness, color and tenacity. The resulting deposits from polymer-based treated system were relatively softer and easier to remove compared to the deposits from either untreated or treated with pH modification. The study of these deposits can also provide an additional decision criteria in selecting the appropriate treatment option.

1 INTRODUCTION

Mineral scaling is considered to be one of the major challenges in harnessing geothermal energy (Brown). In a binary plant, without proper treatment or operational adjustment, an outlet temperature that corresponds to a silica saturation index (SSI) of greater than one will exacerbate scale deposition. It can plug heat exchanger tubes and reinjection pipeline which will lead to generation capacity reduction. The easiest method of preventing silica deposition is to operate at an SSI of close to one or less than one, but the temperature limitation will not capture the full potential of the binary plant. If scaling can be mitigated even at temperature levels corresponding to higher saturation indices, additional electricity can be generated from the heat further extracted.

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.

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).

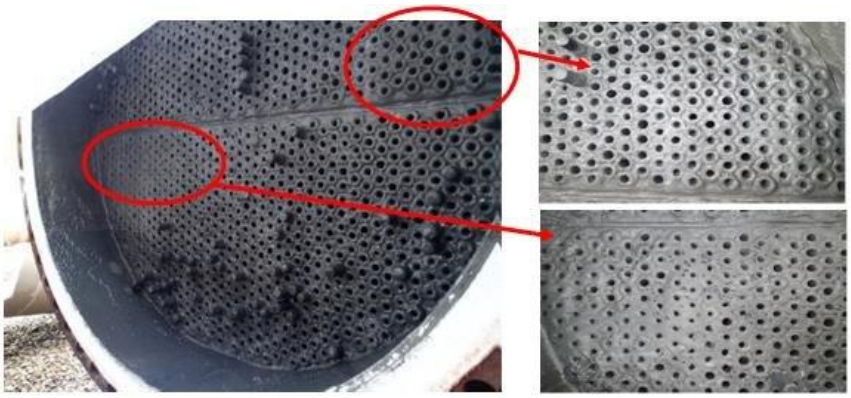


Figure 1. Scaled heat exchanger (vaporizer) tubes that contribute to reduced heat transfer efficiency. Candido and Zarrouk (2017)

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 in 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 brine (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 techniques 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, 1996).

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, 1996).

The aim of this study is to assess the whether different binary plant treatment conditions have an impact on the scaling behavior of the brine. The conditions considered are untreated, pH modified brine and treated with polymer-based scale inhibitor. These conditions were assessed through geochemical simulations, elemental analysis of the actual scales and physical observations like hardness and scale volume.

2 METHODOLOGY/APPROACH

Brine samples used for the study were analyzed using Inductively Coupled Plasma (ICP) spectroscopy. The results were used as input for geochemical simulation using Geomizer™, a proprietary software of Nalco Water. Potential scale forming minerals that are typical to a binary plant were simulated like amorphous silica, metal silicates and metal sulfides. Sample brine analysis is summarized on the table below:

Table 2: Sample brine analysis

Parameters	pH	SiO_2	Al	Cl	K	Ca	Mg	Fe	B	HCO_3	SO_4	Na	As	Sb
Value (ppm)	7.2	729	0.5	4192	386	23.5	0.12	0.32	58.3	32.6	122	2312	3.46	0.08

Actual scale samples coming from these plants were also analyzed to confirm the identity of scales. Both X-ray fluorescence (XRF) and X-ray diffraction (XRD) were done on the samples. Scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM–EDS) was also conducted on some scales.

For physical observations, qualitative hardness and deposit weight densities of the scales were also measured on some samples.

3 RESULTS AND DISCUSSION

Actual scale samples coming from these plants were also analyzed to confirm the identity of scales. Both X-ray fluorescence (XRF) and X-ray diffraction (XRD) were done on the samples. Scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM–EDS) was also conducted on some scales. Geochemical simulation was conducted on sample brine chemistry. The pH of the sample and temperature were varied to help project expected scale forming minerals at both reduced temperature and acidic environment – like pH modification. Saturation indices of different possible scale-forming minerals were calculated, these are amorphous silica, metal sulfides and metal silicates. The results were summarized on the table below:

Table 2: Summary of geochemical simulation under varied brine conditions (projected binary outlet temperature of 100 deg. C)

	Saturation Index	
Brine condition	pH: 7.2	pH: 4.5
Am. silica	2.351	2.444
Iron sulfide	3.326	-7.37
Mg-silicate	1.012	-3.315
Stibnite	Detected	Detected
Orpiment	Detected	Detected
Al-silicate	Detected	Detected

Detected = SI calculated > 100

Geochemical simulation confirmed that common scale-forming minerals are present at both conditions. It can be observed that even with pH modification, the saturation index of silica remains the same with neutral pH. The use of acid does not necessarily change the thermodynamic properties and monomeric silica concentration of the brine. The role of acid is to lower the pH of the geothermal brine, usually at pH 4-5, to delay silica polymerization (Brown, 2013). This can help extract more heat from the inlet brine without causing significant scaling even at lower outlet temperature setting where actual silica concentration is higher than what can

theoretically be dissolved. 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.

Increasing the pH of the system allows silica to be more soluble. As a theoretical comparison, raising the pH of the sample brine to 10 will drop the silica saturation index (SSI) to ~0.4. The same trend was also observed by Brown (2013) using a test case from New Zealand.

Both stibnite (Sb_2S_3) and orpiment (As_2S_3) can deposit if the conditions are correct like pH, availability of sulfide species and temperature. However, typical physical manifestation of stibnite is grayish color. Metastibnite (reddish color) can exist under acidic or oxidized conditions. In geothermal binary plants, these scales are typically observed at the lowest temperature points in the system.

Metal silicates are also minerals of interest as these contribute to the deposition behavior of the system. Metal ions help in increasing the agglomeration rate of colloidal silica particles by acting as bridge.

After geochemical simulation, deposition behavior was observed through inspections spools. Representative samples from different treatment conditions were analyzed using XRF, XRD and SEM-EDS on surface scales. The results of these analyses helped identify if the mechanism of deposition is different depending on the treatment program involved. Three conditions were considered for the study: no treatment, acid dosing targeting pH of 4.5 and using polymer-based silica inhibitor.

From Figure 2, it can be observed that both untreated and acid-treated spools exhibited yellowish to reddish pipe surface color compared to polymer inhibitor dosed condition.

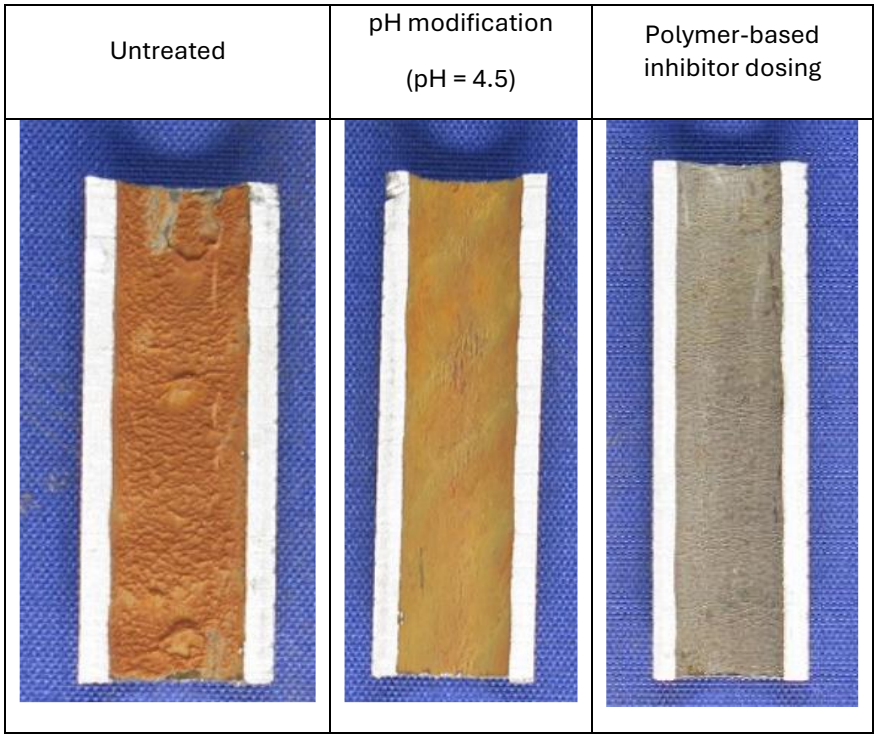


Figure 2: Comparison of inspection spools at different brine conditions (untreated, pH modified, and with polymer-based inhibitor dosing)

The summary of the elemental analyses is shown on the succeeding table. It can be observed that majority of the scale composition of the treated line was amorphous silica while the untreated and pH modified lines was iron. Sulfides in the deposit were also significant in the untreated line and pH modified lines. There is also a considerable percentage 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.

Table 3: XRF and XRD of different brine conditions (untreated, pH modified, and with polymer-based inhibitor dosing)

Untreated	pH modification (pH = 4.5)	Polymer-based inhibitor dosing
SiO2: 72% Fe3O4: 6% SO3: 12% Al2O3: 2% As2O3: 2% K2O: 1%	SiO2: 38% Fe3O4: 41% SO3: 9% Al2O3: 2% As2O3: 1% K2O: 1%	SiO2: 91% Fe3O4: 3% Al2O3: 1%
XRD Significant amorphous material Minor component: magnetite, hematite	XRD Significant amorphous material Minor component: magnetite, hematite	XRD Significant amorphous material

Elemental distribution map of the polymer-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. This complements the XRF results that major scaling components is amorphous silica.

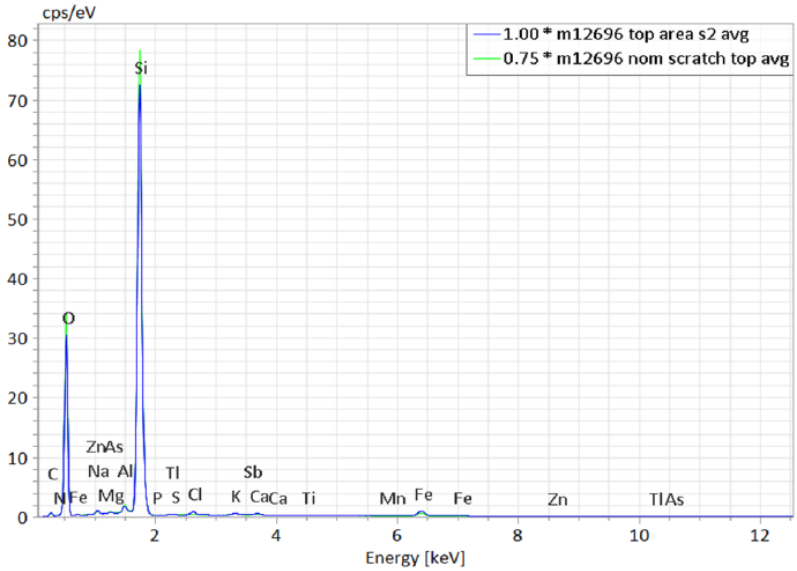


Figure 3: Elemental distribution map of scale under polymer-based inhibitor dosing

Using an actual plant application in Indonesia as an example, physical scale characteristics of polymer-based treated and pH modified brine were compared.

(1)	(2)
	

Figure 4: Actual scale comparison (1) polymer-based treatment (2) pH modification

Focusing on the two treatments involved, pH modification and polymer-based inhibitor dosing, the resulting scales vary significantly in terms of composition and physical characteristics. The scale obtained from (1) was softer and can be easily scraped by hand while the scale formed from (2) was relatively harder and more compact. This supports the theory that changing how the scale forming particles interact through polymer inhibition has a big impact on its scale forming habits compared to delaying the polymerization which is the underlying principle of pH modification.

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:

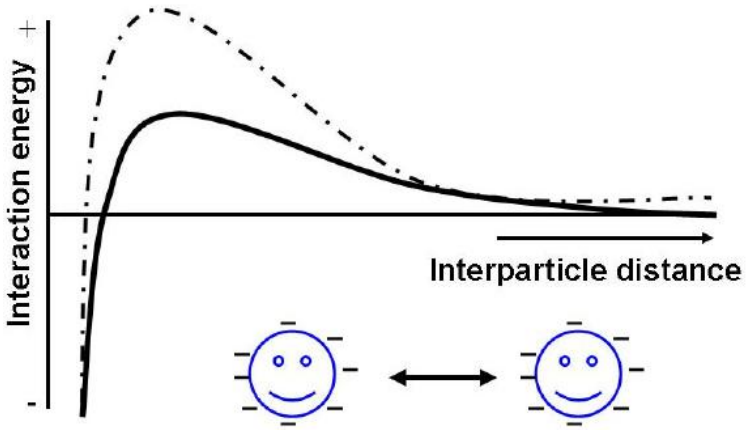


Figure 5: Increase in energy barrier that promotes colloid separation - as illustrated by Brown (2013)

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.

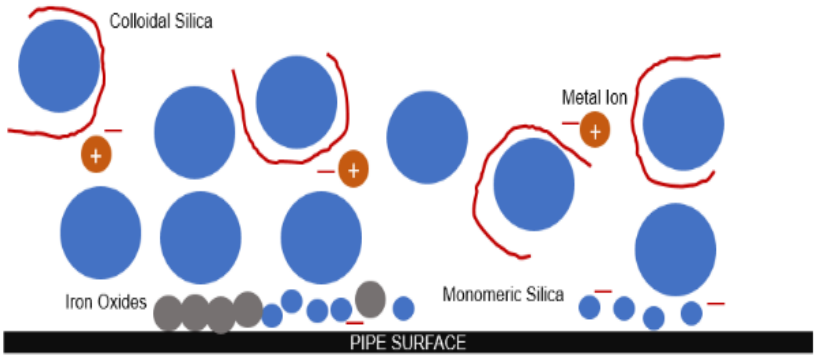


Figure 6: Interactions of polymer-based inhibitor on monomeric, colloidal silica and metal ions in the system.

4 SUMMARY AND CONCLUSIONS

Understanding mineral scaling in a geothermal binary plant can be derived from geochemical simulations, sidestream tests, and real plant operations. The data obtained from these studies can assist in clarifying the scale deposition behavior. This research examines the features of scale deposits created under various binary plant treatment scenarios. The conditions examined included untreated, treated with a polymer-based inhibitor, and treated with modified pH. The gathered scale samples underwent analysis through x-ray fluorescence (XRF), gravimetry, scanning electron microscopy (SEM), and x-ray diffraction (XRD) to identify their mineralogical composition, morphology, and elemental content. Based on the findings, the scales treated with a polymeric inhibitor showed a fairly uniform composition of amorphous silica, predominantly exceeding 90% w/w. Both untreated and treated under pH modification conditions exhibited a mixture of amorphous silica, metal silicates, and metal sulfides. In addition to quantitative outcomes, qualitative observations indicated that the deposited scales vary in physical traits such as hardness, color, and tenacity. The deposits formed from the polymer-treated system were comparatively softer and simpler to eliminate than those from both the untreated system and the pH-modified treatment. Examining these deposits can also offer another criterion for choosing the suitable treatment option.

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