Iron Sulfide Deposition and Inhibition and Its Impact on Geothermal Brine Pumps

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ABSTRACT

In geothermal systems, iron sulfide can be considered as one of the most challenging scales because of the impacts of the deposits formed. This type of scale is usually intermixed with amorphous silica and metal silicates, which in turn, forms tenacious and hard deposits that can be observed in both surface and subsurface facilities. In one case in the Philippines, deposition of iron sulfide along the brine reinjection system negatively impacts the capacity of the brine pump. Aside from scaling along the pipelines, iron sulfide deposition was also observed inside the pump casing which causes the rapid decline of pump capacity. Without operable pumps, the plant is forced to shut down and do manual cleaning to regain normal operations. Dumping of the brine to maintain separator level was also being done because of limited reinjection capacity due to pump capacity decline. Deposition mechanism of iron sulfide was studied, and it was confirmed that existing chemical and mechanical conditions were conducive in the precipitation of this scale. A new inhibition program was studied based on existing cases for metal silicate and sulfide inhibition to check if the same principle can show positive impact on this type of application.

The goal of the inhibition program is to preserve the capacity of the brine pump by minimizing scaling. This will maintain existing or reduce (or to some extent, eliminate) brine dumping rate. It can be observed that before the new inhibition program, the brine dumping rate increases steeply over time. The new inhibition program was able to slow down the steep increase of the dumping rate. This was further demonstrated after the silencer cleaning where it can be observed that the brine dumping rate was consistently controlled for 1 month at 25 kg/s compared to 43 kg/s. Comparing to the baseline, monomeric silica retention increased during the trial which is a good indicator of lesser scaling potential. It was observed that monomeric silica retention increased by 300%. Silica may not be visible in the XRF or XRD analyses because the sample was limited to the brine pump internals only. Aside from quantitative measurements, qualitative observations were also made during the trial. It is worth noting that during an outage were the brine pump was put out of service, no manual barring was done to restart the pump. It was a good indication of the chemical program difference in comparison to the previous experiences of the site.

1. INTRODUCTION

1.1 Iron Sulfide in Geothermal Systems

Mineral scaling in different geothermal systems was proven to be a considerable limiting factor in achieving operational efficiency. It can occur at any location in a geothermal power station where temperature, pressure, pH or velocity changes thereby affecting component concentrations that lead to scaling (Jamero et. al., 2018). Aside from amorphous silica and its derivatives, metal sulfide scaling in geothermal surface facilities can drastically reduce the output of the power plant. The formed hard and tenacious scales can reduce pipeline internal diameter which has severe adverse consequences on both operational and economic considerations (Andritsos & Karabelas, 1995).

Iron sulfide is one of the most common metal sulfide scales found in geothermal systems. It can be considered as the most abundant component in sulfide-rich scales. Observed iron sulfide scales in geothermal can exist in various forms. Geothermal wells in Paris Basin has large dissolved sulfide which forms mackinawite, pyrite and pyrrhotite (Criaud & Fouillac, 1989). A two-phase pipeline in the Philippines showed formation of pyrite and pyrrhotite co-depositing with magnetite and hematite (Jamero et. al., 2018). Another crystalline phase identified and observed in a geothermal facility in the US is troilite (Gallup et al., 1990). Among the crystalline phases observed, pyrite can be considered as the most stable phase. At relatively high temperatures conditions of 200 °C and above, pyrite and pyrrhotite are the dominating structures while other metastable sulfide phases can exist at lower temperatures and atmospheric conditions (Taylor, 1980).

Like mineral scaling in general, iron sulfide scaling is affected by both thermodynamic and kinetic considerations. Factors like flow velocity, pH and concentration of scale-inducing species (supersaturation) have high contribution on the scaling potential.

1.2 Factors Affecting Iron Sulfide Formation

According to the study of Andritsos & Karabelas (1995), aside from saturation conditions, pH, flow velocity and temperature have varying effects on the deposition behavior of iron sulfide. In terms of pH, the observed deposition behavior (assuming constant species concentration, temperature, salinity and velocity), resembles a “bell” shape curve with peak at pH 6.2.

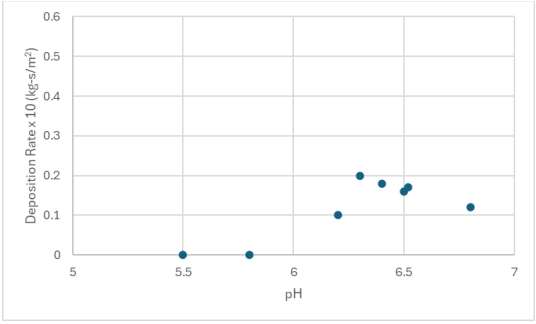

Figure 1. Effect of pH on deposition rate of iron sulfide. Reference: Andritsos & Karabelas, 1995)

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1.3 Geothermal Brine Pump Deposition

A geothermal site in the Philippines experiences brine pump capacity decline due to mineral scaling. Without enough capacity, diversion of the brine to the reinjection system can be challenging. To maintain the level inside the separator vessel, dumping of brine to collection ponds is being done. In worst case, production wells are being shut or throttled to manage limited reinjection capacity.

The nature of the deposition was studied by getting actual samples from pump casing and impeller. Figure 2 shows the actual scale samples obtained and analyzed.



Pump Casing	Impeller

Figure 2. Actual scale samples obtained and analyzed from the brine pump.

The samples were submitted to an analytical laboratory in Singapore for X-ray Fluorescence (XRF) and X-ray Diffraction (XRD) analyses. Below is the summary of the analyses:

Downstream Deposit Analysis

Elemental Analysis by X-ray Fluorescence — **Test Method: CP17000**

The sample preparation was: Dried at 105 °C

Iron (Fe)	50 wt %
Sulfur (S)	47 wt %
Arsenic (As)	1 wt %
Copper (Cu)	1 wt %

Total From XRF: 99 wt %

The following elements were not detected or were below the reporting limit (< 0.5%):

Al Sb Ba Bi B Br Cd Ca Ce Cs Cl Cr Co Dy Er Eu F Gd Ga Ge Au Hf Ho In I Ir La Pb Li Lu Mg Mn Hg Mo Nd Ni Nb Os Pd P Pt K Pr Re Rh Rb Ru Sc Sm Se Si Ag Na Sr Ta Te Tb Sn Tm Ti W Tl Th U V Yb Y Zn Zr

Analysis by X-ray Diffraction

The XRD was performed on: Dried at 105 °C

Iron Sulfide (Pyrite) - FeS2

Some amorphous material present.

Figure 3. XRF and XRD analyses of the scale samples obtained from the brine pump.

The primary identity of the scale is iron sulfide (pyrite) which explains the general dark gray color of the scale. This type of scale was also observed in other geothermal facilities like Leyte, typically from mixing an acidic well which carries the iron ions and a neutral well which causes the increase in prevailing pH (Jamero et al., 2018). Analysis of the brine that passes through the brine pump is shown below:

pH	Cl	Fe	H2S	SiO2	Mg	Na	SO4
6.4	10621	0.02	2.2	730	0.22	5951	26.4

The actual brine pH is around 6.4. Based on Andritsos & Karabelas (1995) and as confirmed with our site experiences, pH is considered as the main driving factor of iron sulfide scaling. The pH of the brine is within the pH range of 6 to 6.8 at which this scale is expected to precipitate. Concentration of scale forming ions is also an important factor to consider, especially for systems that we are expecting an influx of iron.

2. METHODOLOGY

From a similar site experience on addressing iron sulfide scaling, the same program principle was proposed. The program focuses on addressing the metal-based scales and preventing potential metal silicate formation both in the brine pump internals and downstream pipeline. This may help maintain the overall capacity of the pump.

In this case, a combination of metal silicate/sulfide/oxide inhibitor blend was used alongside with a silica inhibitor. These chemistries were blended on-site into a single product and dosed upstream of the brine pump. The details of the chemical program are summarized below:

Chemical	Function	Target Dosage
GEO981	Minimizes monomeric silica deposition by crystal structure modification and colloidal silica dispersion.	5 ppm
GEO962 and GEO939	Inhibition of metal silicates/sulfides/oxides to prevent further co-deposition with amorphous silica forming much harder scales.	10 ppm

The proposed program was dosed for a period of 4 months. Brine dumping rate was the main key performance indicator involved. Ideally, the program should maintain the initial dumping rate to say the inhibition performance is favorable.

3. RESULTS

For the trial, key indicator that were agreed upon are reduction in the increase of dumping rate which ultimately will have an impact on the actual time in-between cleaning of the brine pump. To gain additional data during the trial, monomeric silica was also measured. Scaling coupons were also installed both upstream and downstream of the brine pump.

The trial started last Oct. 19 with a target 4-month run which will end on Feb. 19, 2024. During the testing, several outages were encountered which affected the trial. One was from Nov. 9 to Nov. 17 due to dosing pump issues and the other one was from Dec. 5 to Dec. 17 for silencer dump cleaning.

The succeeding graph shows the brine dumping trend from September 15, 2023 to January 22, 2024:

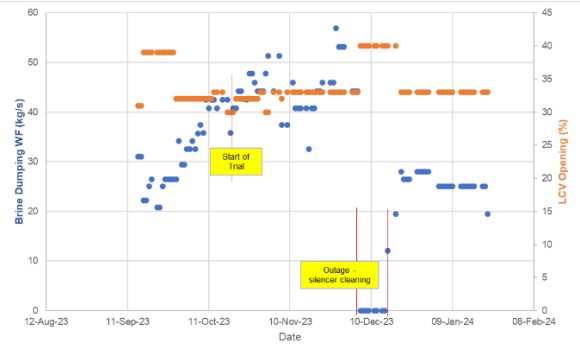


Figure 4. Brine dumping rate before and during the trial.

The program has started under an existing dumping condition. It can be observed that before the new inhibition program, the brine dumping rate increases steeply over time. The proposed program was able to slow down the steep increase of the dumping rate. This was further demonstrated after the silencer cleaning where it can be observed that the brine dumping rate was consistently controlled for 1 month.

Aside from brine dumping data, monomeric silica levels were also monitored during the trial.

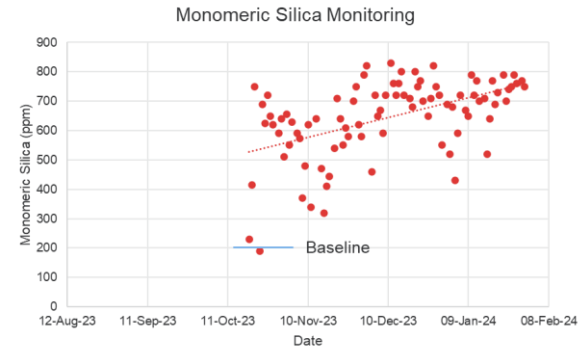


Figure 5. Monomeric silica levels along the brine pump line

Plotting the silica saturation index of the brine going to the brine pump at several temperatures, it can be observed that after the separation unit, the brine is already supersaturated with respect to amorphous silica. Exit temperature was estimated to be around 150 deg. C.

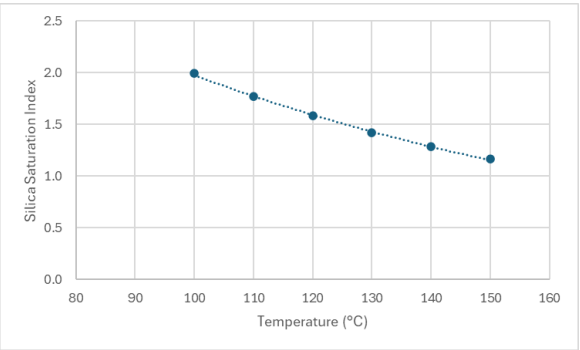


Figure 6. Calculated silica saturation index (SSI) at various temperatures.

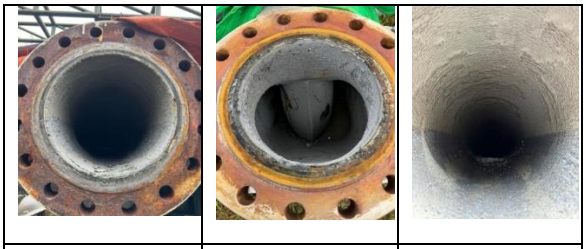
Theoretically, amorphous silica should start to precipitate along the brine line after the separator. However, the brine pump scale XRF and XRD showed no trace of amorphous silica. A possible explanation to this is even at supersaturated conditions, the size of colloidal silica might not be big enough to precipitate out of the solution. Both thermodynamics and kinetics of amorphous silica scaling affect the scaling tendency (Brown, 2011). It was observed also that the travel time of the brine from the separator outlet to the brine pump is less than 10 seconds which might not be enough for colloidal silica to form even at supersaturated conditions. Deposition of amorphous silica generally follows to mechanism, direct monomeric silica deposition and colloidal silica formation with subsequent precipitation (Brown, 2011). From the result of monomeric silica monitoring, the baseline monomeric silica is low which means that silica has started to polymerize but the conditions are not enough to form large colloidal particles for deposition to happen. According to Dixit et al. (2016), for turbulent flow conditions, the favorable mode of scaling is monomeric silica deposition assuming that there is available surface for deposition. On the other hand, laminar or quiet conditions are favorable for silica polymerization. Since the brine pump hydrodynamic condition is turbulent, direct monomeric silica deposition is favored; however, iron sulfide and magnetite where already formed inside the brine pump internals which limits the condition for direct monomeric silica deposition to happen.

Comparing with the baseline, monomeric silica retention generally increased during the trial which is a good indicator of lesser scaling potential downstream of the treated system. Amorphous silica may not have precipitated inside the brine pump but considering the baseline monomeric silica without treatment, it is expected that deposits will be observed downstream. The treatment program may minimize possible amorphous silica downstream of the brine pump and in the reinjection lines.

Scale coupons were also used to monitor the progress of the trial, but the data can be considered as inconclusive since there was an outage during one of the observation periods. Here is the summary of the measurements:

	Days In	Initial Weight (g)	Final Weight (g)	Remarks
Baseline 1 (BP – B)	15	25.2	27.9	Inserted without BP-B cleaning
Baseline 2 (BP – A)	31	27.3	28.5	Started clean
Program	33	27.2	28.8	Inserted without BP-A cleaning; with 9 days outage

Aside from quantitative measurements, qualitative observations were also made during the trial. It is worth noting that during an outage were the brine pump was put out of service, no manual barring was done to restart the pump. It was a good indication of the chemical program difference in comparison to the previous experiences by the site.



Upstream	Brine Pump Internal	Downstream

Figure 6. Brine pump inspection after the 4-month trial run.

According to the studies done by Andritsos and Karabelas (1995), the brine condition is favorable in the formation of iron sulfide. It can be considered that saturation conditions as well as pH are the main driving factors for the deposition. In comparison to the dosing behavior along the lines and inside the brine pump, it was observed that iron sulfides where mainly deposited inside the brine pump and combination of iron sulfides and amorphous silica scaling was present on the upstream and downstream pipelines. The hypothesis is that iron sulfide deposition is more pronounced inside the brine pump due to turbulence. Turbulent structure of the flow enhances particle interaction and increases agglomeration (Afkhami et al., 2019).

4. CONCLUSIONS AND RECOMMENDATIONS

The condition inside the brine pump as well as the brine characteristics are contributing factors to the deposition of iron sulfide. General dispersion and inhibition were considered for the selection of a suitable treatment program. Quantitative and qualitative results show that the new program used in brine pump line scale inhibition is promising. The positive impacts of the program were observed firsthand. These are related to maintaining the dumping rate prior to the start of the program and obvious differences like elimination of manual barring.

Ideal scenarios for the conduct of the program are the following:

1. The dosing program should ideally start with a clean system – to be able to fully demonstrate the inhibition capabilities. Pre-existing scales usually serve as seed for other scales so this can have an impact on the metrics being measured.

2. Brine dumping should be eliminated prior to the start of the dosing program. This will help to clearly demonstrate the benefits of having a preventive approach.

3. Brine sampling point should be available downstream of the brine pump. This will capture the true monomeric silica retention and be able to relate scaling downstream of the system.

4. Scale coupons should be installed on a clean system prior to the start of the program.

In relation to item 2, there was an observation of soft white deposits at the dump area of the silencer. Based on initial XRF results, these are purely amorphous silica. Compared to previous deposition behavior, these white deposits are easier to clean and does not form hard deposits. However, the deposition rate is faster compared to the conditions before. This can be attributed to the further concentration of silica downstream of the silencer which forces the inhibitor-colloidal silica bonds to be unstable. The result is precipitation of amorphous silica instead of complexing with metal ions. This leads to a strong recommendation that the inhibitor program should be dosed in systems where we will not expect re-concentration (exposure to atmosphere/flashing) and drastic temperature reduction that will increase the applicability beyond the allowable saturation index range.

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REFERENCES

Afkhami, M. et al.: Effect of Reynolds number on particle interaction and agglomeration in turbulent channel flow. *Powder Technology*, Vol. 343, 908 – 920. (2019).

Andritsos, N. and Karabelas, A. J.: An experimental study of sulfide scale formation in pipes. *World Geothermal Congress Proceedings 1995*, Firenze, Italy, 2469 – 2474. (1995).

Andritsos, N. and Karabelas, A.J.: Sulfide scale formation and control: the case of lead sulfide. *Geothermics*, Vol 20, 343 – 353. (1991).

Brown, K.: Thermodynamics and kinetics of silica scaling. *Proceedings International Workshop on Mineral Scaling*. (2011).

Criaud, A. and Fouillac, C.: Sulfide scaling in low enthalpy geothermal environments: a survey. *Geothermics*, Vol 18. 73 – 81. (1989).

Dixit, C. et al.: Experimental study on the kinetics of silica polymerization during cooling of the Bouillante geothermal fluid (Guadeloupe, French West Indies). *Chemical Geology*, Vol. 442, 97 – 112. (2016).

Gallup, D. et al.: Heavy metal scaling in production well at the Salton Sea geothermal field. *Geothermal Resources Council Transactions*, Vol. 15, 1583 – 1590. (1990).

Jamero, J., Zarrouk, S. J. and Mroczek, E., 2018: Mineral scaling in two-phase geothermal pipelines: two case studies. *Geothermics*, Vol. 72, 1 – 14. (2018).