Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

Inhibiting Complex Deposits in Geothermal Energy Extraction

Jasbir S. Gill, Ph.D.

Water Energy Solutions Inc 2219 Skylane Drive, Naperville, IL 60564, USA

Thewesinc@gmail.com

Keywords: Scale inhibitors, mixed mineral deposits, silica-silicates of Fe, Al, Mn; Stibnite, Sulfide-silica- silicate deposit, deposit formation and inhibition mechanisms.

ABSTRACT

Earth has a vast amount of heat stored at its center, this inexhaustible resource is expected to last billions of years and is constantly available, which can produce energy as base load, 24/7, 365 day a year. Several other competing renewal resources of energy such as, solar, wind, thermal, etc., has many limitations, however, are gaining wide use. Use of geothermal energy is also limited due to the formation of complex deposits in various parts of the geothermal energy extraction processes. Effective scale and corrosion inhibition can result harvesting more energy from geothermal fluids in addition to protecting geothermal assets. Dealing with deposits consisting of Fe, Mn, As, either with silica or sulfide or their mixtures require strategies beyond threshold inhibition of such minerals. In this paper the author has presented recent improvements in understanding of complex deposit mineral formation and the use of chemical inhibitors for geothermal brine treatment to extract maximum enthalpy from the geothermal resources.

1. INTRODUCTION

The chemistry of geothermal fluid is an important factor in exploration, development, and utilization of geothermal resources. In the exploration phase, geochemistry is used to evaluate the origin of the water, to estimate underground temperature, characterize the reservoir chemistry with respect to utilization and to define environmental impact of the utilization. Most of the earlier scale control was limited to inhibiting calcium carbonate in the production wells and silica in the surface equipment. However, due to the unusual brine chemistry of Salton Sea and similar geothermal fields, other scales such as iron silicates, iron sulfide, antimony sulfide, barium sulfate, calcium sulfate, calcium fluoride, etc., have been documented. Most common mitigation of silica deposit is done by modifying the pH of the brine, known as pH-mod. Some of the data from Salton Sea showed that pH has to be adjusted to ~3 in order to prevent silica-based deposit, when the brine was in equilibrium with atmosphere (Gallup,1998). Both silica deposit control and plant asset preservation should be the drivers while using pH mod and requires a delicate balance of corrosion and silica deposit control.

Process of adding acid (pH MOD) to mitigate silica may result in corrosion and the formation of other scales, which are formed at lower pH, such as stibnite and various other sulfides of iron, manganese and arsenates, etc. In a recent publication (Gill, 2020) summarized the earlier literature on the use of organic molecules and their failures for silica inhibition. The earlier literature became a great hurdle in the application of organic molecules for managing silica deposits. Dealing with deposits consisting of Fe, Mn, As, either with silica or sulfide or their mixtures require strategies beyond threshold inhibition of such minerals. In this paper the author has presented recent improvements in understanding of complex deposit mineral formation and the use of chemical inhibitors for geothermal brine treatment to extract maximum enthalpy from the geothermal improvement.

The author has taken a new holistic approach to mitigate scale and corrosion based on examining the entire process cycle, starting with brine in the production phase in the ground until it is sent back to the ground through injection well. As the brine moves through the production well, understanding the impact on scale and corrosion from geochemical changes in the production well; modifications in temperature, pH, and brine concentration during brine flashing; and pH adjustments to prevent scale and corrosion. The deposit mitigation for mixed scales is based on the mechanism of formation of complex deposits and the appropriate formulation composition of the scale inhibitor molecules to block the pathway to deal with such deposits.

2. RESULTS AND DISCUSSION

Geothermal Energy as a renewable source is once again getting very popular and can favorably compete with wind and solar. In a recent Power Magazine, dated November 19, 2020, podcast “Could geothermal energy become the sexy renewable”. This podcast is about a successful field demonstration of a new technology called Closed-Loop Geothermal Technology developed by GreenFire Energy. This technology is very cost effective as it does not require drilling of new wells. Furthermore, it can use geothermal or oil wells that are abended due to either low permeability or high non-condensable gasses or non-producing oil wells. Moreover, since it is a closed-loop system that requires very little maintenance.

Currently, however, most of the geothermal energy is produced using either flash units, or binary or a combination of flash and binary systems. These systems heavily depend on management of scale and corrosion. Since the earlier work of Harrar (Harrar, et.al.,1978,1979,1982) and Gallup (Gallup, 2005), there has been a great deal of progress and advances made in understanding of the mechanism of the formation of complex deposits and new tailor-made scale/deposit inhibitors.

However, based on their laboratory studies there is still a stigma against the use of organic scale inhibitors, especially for silica/silicate and other highly insoluble minerals. Let's first understand how these complex deposits are formed, which can be helpful in the use of right strategies and molecular compounds and their formulations to mitigate most of the deposits.

2.1 Advances in Understanding of Complex Deposit Formation in Geothermal System:

Brine chemistry starts to change as the brine moves upwards in the production well, then the brine chemistry further undergoes changes in flash units, binary exchangers and in the in the injection well. Internal flashing in the production well causes the brine pH increase, which is responsible for calcium carbonate scale as well as may produce two phase fluid responsible for corrosion. In flash or steam separator units, the loss of steam fraction causes brine to concentrate and cool down, and escape of non-condensable gasses results in increased pH; such changes will cause scaling, especially silica precipitation. Silica deposit is caused as a result of its polymerization, co-precipitation with other minerals, precipitation with many multivalent ions, and monomeric silica deposition on the surface of the heat exchangers. Several of these processes may take place concurrently, making it difficult to predict equilibrium solubility. To prevent silica-based deposit, it is essential to control all these paths, simultaneously (Gill,1993,1998). Amorphous silica solubility is not well defined (Iler, 1979) as a thermodynamic quantity K_{sp} like most other sparingly soluble minerals, which are often encountered in scale deposit. The solubility depends on many variables, such as rate of precipitation, kinetic energy of the fluid, and the presence of seed crystals and since it is an amorphous material, the seeded-growth does not require any lattice match with the seed/substrate. Deposit is often found at the points of turbulence such as bends in the pipelines and while, there may not be any deposit on sections of the pipeline with no turbulence (Gill, 2011). In reality these deposits, which are referred as silicates of iron, aluminum, zinc, etc., may not represent well-defined compositions and K_{sp} as ionic compounds e.g., calcium carbonate or calcium sulfate. There are some obvious reasons for poor definition of the composition of such silicates precipitated in real time in geothermal systems.

Formation of these complex minerals is most likely the result of coprecipitation of metal ions or their hydrates or even highly insoluble minerals such iron sulfide, arsenic sulfide, antimony sulfide, etc. with silica (amorphous silica). This results in decreasing the equilibrium solubility of silica as well. Based on the aforesaid reasons, these complex-deposit forming minerals widely differ from deposits that are caused by simple ionic compounds, such as calcium carbonate. A strategy to inhibit these complex minerals requires a new approach than typical threshold inhibitors used in the past. One thing is certain, that the earlier laboratory studies (Gallup, 2005) has shown that very insoluble minerals, such as calcium phosphate, silicates of iron, manganese, aluminum, and sulfides of antimony, iron, and arsenates show poor threshold inhibition using threshold inhibitors, which is not surprising. There are several mechanisms that may come into play to mitigate the fouling caused by these minerals.

1. Threshold inhibition, where all the scale forming ions stay in solution
2. The precipitated material can also be dispersed due to the following changes caused by the addition of the chemical additives (inhibitors)
    a. Change the surface potential (ζ potential) of the precipitated particles (Hann et.al, 1993) mostly more negative to prevent adherence on the negatively charged surfaces (negatively charged metal surfaces) similar to Brownian motion.
    b. Change the particle size to smaller size that can be easily dispersed
    c. Prevent co-precipitation by inhibiting the seed formation, such as precipitation of other minerals, hydrolysis of the metal ions, etc.
    d. Chelation of the metal ions such as Al, Mn, Fe, Zn, etc.
3. In addition to or in lieu of the organic scale inhibitors, deposits can be mitigated using the following
    a. Acidification of the brine to retard the kinetics of silica polymerization
    b. Removal of the scale forming species such as Silica (CRC technology or other methods)
    c. Keeping the brine temperature above the supersaturation of amorphous silica

The author has observed in the laboratory and in the field application that highly insoluble minerals (K_{sp} $<1.0\mathrm{X}10^{-12}$; e.g., K_{sp} for Stibnite is ~ $1.6\mathrm{X}\ 10^{-91}$) are highly unlikely to prevent from precipitation (threshold inhibition); such minerals need to be managed using dispersion as outlined above in mechanism number 2. These dispersants are usually polymers or copolymers with high charge density. The data in table 1 show that threshold inhibitors for antimony sulfide are not as effective as dispersants. During the laboratory study, mixing of very dilute solutions of stannic chloride and antimony sulfide results in an instant precipitation, even in the presence of threshold inhibitors. The dispersion is measured using % transmittance and compared to the control test condition. In this case a copolymer of acrylic acid and sulfonated carboxylic acid gave the best results for preventing stibnite deposition.

Table 1. Dispersion of Antimony sulfide

Inhibitor	Inhibitor Concentration active PPM	% Dispersion	
		pH 7.5	pH 5.5
Phosphonate, Threshold Inhibitor	5	57	45
Blend of two Carboxylic acid Polymers	5	93	57
Copolymer of two Carboxylic acid Monomers	5	95	63
Copolymer of Carboxylic acid Monomer and a Sulfonated Carboxylic	5	97	72

As shown in Figure 1, the most favorable conditions for stibnite precipitation are low pH and lower temperature.

1. Highly Insoluble Mineral
    - ✓ Ksp = 1.6E-91 (ref. Calcite KS = 4.45E-09)

P

1. Strong Relationship with pH and temperature
    - ✓ Supersaturated at 90 °C at pH<9.7
    - ✓ Supersaturated at,195 °C and pH ~5.96

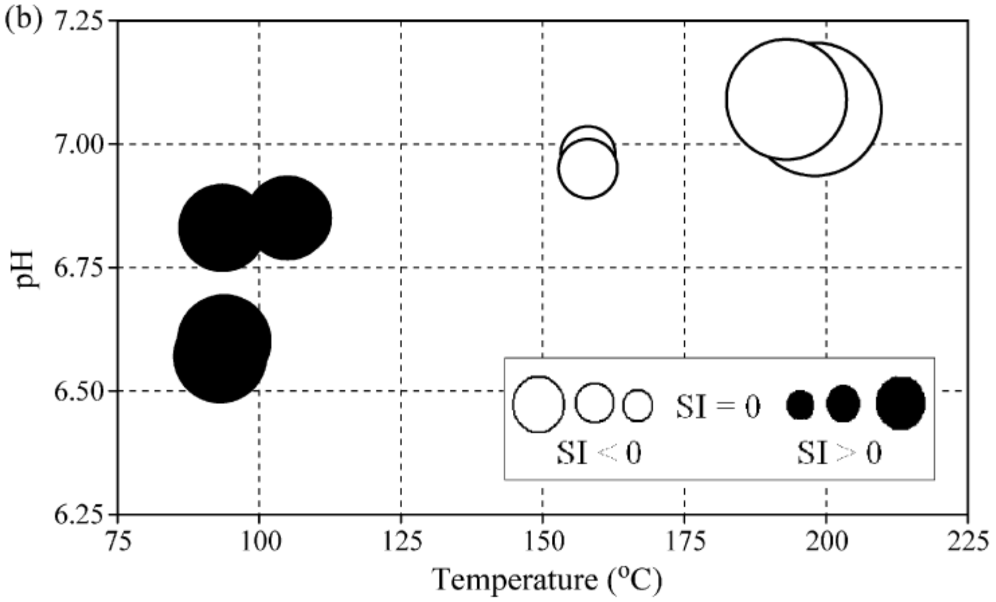
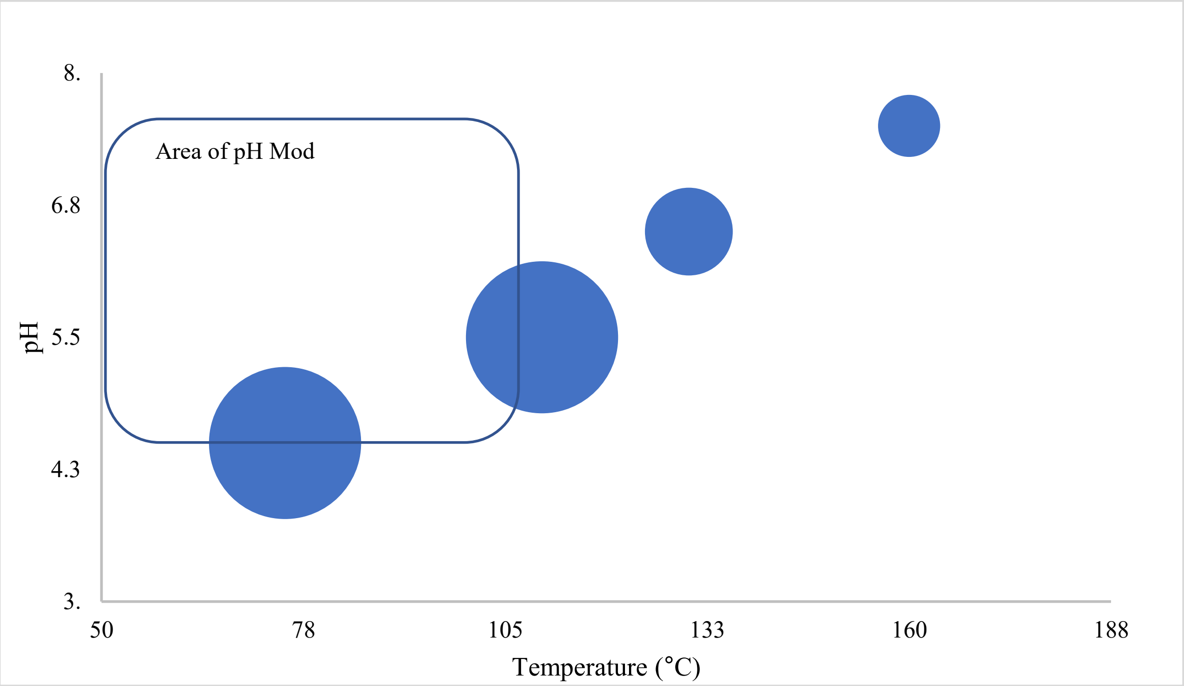


Figure 1. Stibnite equilibrium as a function of pH and Temperature (Ref: Nathaniel Wilson, et.al., Geothermics 36 (2007) 330–347

Such conditions generally result from cooling down of the brine (after flashing, binary units, and injection wells) and addition of acid to control silica precipitation, since silica also tend to precipitate in colder brine. In geothermal systems where there is a potential for brine to be supersaturated with respect to mineral such as Stibnite or other sulfides in addition to amorphous silica, pH Mod may not be very helpful. As shown in Figure 2, pH range for pH-Mod can be from pH 4-6 but preferably <5. This pH range and lower temperature overlaps the conditions of supersaturation of sulfide scale, especially antimony sulfide. Gill and coworkers (Gill, et.al., 2018) presented a case study where the results showed that in the binary power plant, pH mod helped prevent the formation of silica deposit, however, the lower pH and lower temperature conditions made it ideal for the formation of antimony sulfide deposit (Gill, et.al., 2013). In the absence of pH Mod, the brine pH was ~8.0 and the plant never observed antimony sulfide. The power plant has the option of using antimony sulfide inhibitor and continue with pH Mod. As shown in Table 1, most effective scale inhibitors are anionic polymers or small molecule and generally require neutral to alkaline pH to function. Performance of several scale inhibitors shown in this study lose their performance significantly at lower pH. The stibnite dispersant does work at pH 5.5 but it will require higher dose as compared to the dose at pH 7.5 or 8, adding extra cost to the treatment. Moreover, very insoluble minerals like stibnite with K_{sp} of 1.6E-91 can only be dispersed rather than threshold inhibition.

Stibnite Precipitation and pH Mod

Figure 2.



Precipitation of Stibnite as a Result of pH Mod to Control Silica Deposit

The other option would be the use of silica inhibitor without lowering the pH. The Plant decided to use the silica inhibitor and not use pH mod, which prevented the deposition of both silica and antimony sulfide; higher pH kept antimony sulfide below saturation level. The power plant also reaped additional advantages such as, no acid handling, acid cost savings, and lowering corrosion. Based on the mechanism of complex deposit formation, a custom solution can provide multiple advantages including lowering total cost of operation.

In another similar geothermal power plant where the complex deposit consists of iron sulfide, iron silicate and amorphous silica, neither the traditional dispersants nor silica inhibitor could completely mitigate the fouling in the geothermal power plant. The deposit composition showed predominantly silica and the application of silica inhibitor did show improvement in fouling by controlling silica deposition, however, lower silica contents in the deposit revealed the presence of ~20% iron sulfide. A combination of dispersant and the silica inhibitor gave far better performance than the individual components. (Mantri, et.al., 2018).

2.2 Advances in Inhibitor Chemistry and their Application:

Products that are not compatible with the brine chemistry become part of the problem rather than part of the solution. Gallup in his laboratory studies with organic inhibitor observed more deposit in the presence of some of the scale inhibitors than in the absence of any inhibitor (Gallup, 2005). There can be several reasons for the observed behavior from some of the organic molecules.

1. The molecule forms a polysalt with any of the species in the brine and act as seed material.
2. Poor hydrothermal stability of the molecule may result in degradation of the product, causing seeding to precipitate scale forming minerals
3. Copolymer may have an unreacted monomer, which forms salts with brine components
4. There may be unreacted or access of chain transfer/initiator such as bisulfite, which precipitates with calcium or other cations in the brine. Such solids are capable of further seeding other minerals, in addition to causing fouling.

5. Polymer or copolymer may not have the right molecular weight resulting in its precipitation
6. The inhibitor molecule, especially the copolymer may not have a proper Hydrophilic Lyophilic Balance (HLB), causing its non-compatibility.

Most of the commercially available silica inhibitors performed poorly as threshold inhibitor prior to the invention of Acumer 5000, a terpolymer with composition Poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid: no-ionic), by Hahn and coworkers (Hann, et.al.,1994). The mechanism of inhibition for silica-based deposit with Acumer 5000 was based on increasing the negative surface charge of the silica particles and thus repelling the highly negatively charged particles from the heat exchangers (Hann, et al.,1993). A combination of the silica inhibitor (a low molecular weight copolymer of anionic monomer with no-ionic monomer) with a dispersant at neutral to slightly alkaline pH has been found very effective in controlling amorphous silica, silicates of iron, aluminum, manganese and combination of silica coprecipitated with sulfide scale such as antimony and iron. Padilla and coworkers reported excellent results (Padilla, et.al., 2005) from their trial of pH mod and organic inhibitors. One of their finding is worth mentioning here that at Berlin geothermal field they were able to reduce the brine injection temperature from 184 ^{0}C to about 160 ^{0}C without concern for silica scaling. This would be sufficient to power a binary plant of about 5 MW size.

Deposit control also impinges on corrosion control since most of the corrosion products will directly or indirectly get involved in the precipitation of deposit causing minerals. pH Mod can be a source of corrosion, which must be weighed in when comparing the cost of acid versus the organic scale inhibitor. In some of the brines, pH Mod may trigger the formation of Stibnite and other sulfide scales and that should also be considered during treatment assessment. Removal of Stibnite, other sulfides, and arsenates poses great hazards to the environment and the workers. Acid wells, especially sour brines are very corrosive to the well lining. These wells are often treated by adding caustic to the well and then subsequently acid is added to combat silica precipitation. There may be an alternate solution to inhibit corrosion using some of the corrosion technologies (Gill, et al. 2010, 2017, 2019) used in the oilfield sour wells. Acidification of high sulfide brine may also generate H_2S causing pollution and possibly sulfur deposits if the condensate is used in direct contact cooling system. All these challenges should be carefully evaluated before selecting the mitigation of deposit and overall geothermal brine treatment.

3. CONCLUSIONS

Most of geothermal plants have unique designs based on the geothermal field enthalpy and the brine chemistry of the resource. A well thought management of scale and corrosion control as a total strategy using holistic approach can protect plant asset and enhance the energy production. Over the last twenty years, great advancements have been made in both understanding the complex mineral formations and their inhibition with the use of tailor-made organic molecules. Controlling corrosion of acid wells may be more cost effective by using corrosion inhibitors than the current practice of caustic addition. The cost comparison of the treatment with acid or caustic versus the chemical inhibitors should include the total cost of corrosion and fouling and handling of acid and caustic in terms of safety of the workers and environmental pollution.

4. REFERENCES

Gallup, D.L.: Brine pH Modifications Scale Control Technology, GRC Transactions Vol.20 (1998).

Gallup, D.L.: Aluminum Silicate Scale Formation and Inhibition (2) Scale Solubilities and Laboratory and Field Inhibition Tests, *Geothermics* 27, 485 (1998).

Gallup, D.L: Investigation of Organic Inhibitors for Silica Scale Control in Geothermal Brines, *Geothermics* 31,415(2002).

Gallup, D. L., and Barcelon, E.: Investigations of Organic Inhibitors for Silica Scale Control from Geothermal Brines-II, *Geothermics* 34, 756 (2005).

Gill, J.S.: Method for Controlling Silica/Silicate Deposition in Aqueous Systems using Imines, U.S. Patent 4,874,527 (1989).

Gill, J.S., Rey, S.P., and Wiernik, J.H.: Method of Controlling Silica/Silicate Deposits in Aqueous Systems using Phosphonates and Carboxylic/Sulfonic polymer, U.S. Patent 4,933,090 (1990).

Gill, J.S.: Inhibition of Silica-Silicate Deposits in Industrial Water, Colloids and Surfaces 74, 101 (1993).

Gill, J.S.: Silica Scale Control, Paper No. 226, CORROSION/98, NACE International, Houston, TX (1998).

Gill, J.S., Gallegos, M.A., and Jacobs, G.T.: Effective Chemical Inhibitors for Corrosion Control in Geothermal Processes Especially Geysers and pH Mod systems, GRC Transactions Vol 34(2010).

Gill, J.S., Jacobs, G.T.: Development of New Silica Inhibitor- Laboratory and Field Study, GRC Transactions Vol 35(2011).

Gill, J.S., Muller, L., and Rodman, D.: Inhibition of Antimony sulfide (Stibnite) scale in Geothermal Fields, GRC Transactions Vol.37(2013).

Gill, J.S.: Mitigation of Corrosion in Geothermal Systems, U.S. Patent 9,688,903 (2017).

Gill, J.S., and Jacobs, G.T.: Managing Silica Deposits in Geothermal Power Plants- Pros and Cons of pH Mod versus Silica Inhibitor, GRC Transactions, Vol. 42(2018).

Gill, J.S.: Mitigation of Corrosion in Geothermal Systems, U.S. Patent 10,246,629 (2019).

Gill, J.S.: Improvements in Geothermal Deposit Control- Advances in Understanding and Identification of Unusual Minerals and new Scale Inhibitors, GRC Transaction Vol 44(2020).

Hann,W.F.,Robertson,S.T., and Bardsley,J.H.: Recent Experience in Controlling Silica and Magnesium Silicate Deposits with Polymeric Dispersants, IWC- 93–5, International Water Conference, Pittsburgh, PA.(1993).

Hann, W.M., Bardsley, J.H., Robertson, S.T., and Shulman, J.E.: Silica Scale Inhibition, U.S. Patent 5,277,823 (1994).

Harrar, J.E., Lorensen L.E., Otto, C.H. (Jr.), Deutscher, S.B., and Tardiff, G.E.: Effects of Organic Additives on the formation of Solids from Hypersaline Geothermal Brine, GRC meeting, Hilo, Hawaii, July(1978).

Harrar, J. E., Locke, F. E, Otto, Jr., C. H, Lorensen, L. E. and Frey, W. P.: On-line Tests of Organic Additives for the Inhibition of the Precipitation of Silica from Hypersaline Geothermal Brine II. Tests of Nitrogen-Containing Compounds, Silanes, and Additional Ethoxylated Compounds, UCID-18195 (1979).

Harrar, J.E., Lorensen, L.E., and Locke, F. E.: Method for inhibiting silica precipitation and scaling in geothermal flow systems, US. Patent 4,328,106 (1982).

Iler, R. K.: The Chemistry of Silica*,* John Wiley & Sons, New York.(1979).

Mantri, D., and Gill, J.S.: Iron Sulfide Scale Control Agent for Geothermal Wells. U.S. Patent Application 0327294 (2018).

Padilla, S. R., Barnett, P., Castro,M., Guerra, E., and Henriqez, J. L.: Silica Polymerization and Deposition Trials at the Berlin Geothermal Field, El Salvador, Proceedings World Geothermal Congress(2005).