MAXIMIZING GEOTHERMAL POWER PRODUCTION BY CONTROLLING SCALE AND CORROSION IN GEOTHERMAL SYSTEMS

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ABSTRACT

Corrosion and scale formation in various parts of geothermal systems increase the cost and limit power production. Corrosion can be induced by hot brine that may contain sulfide, carbon dioxide or addition of acid to inhibit silica precipitation. Scale formation due to calcium carbonate, calcium sulfate, calcium fluoride, silica/silicates, iron oxides, and sulfides of antimony or arsenic, often limits brine flow and decreases heat transfer, requiring costly cleaning operations and reducing power generation. This paper highlights various challenges and outlines chemical solutions to deal with the challenges, based on laboratory and field experiences. Inhibition of scales such as silica and stibnite that are formed at low temperature can enable the capturing of more energy by using additional flashes and binary systems.

INTRODUCTION

As climate change is now widely acknowledged as a major threat to the planet and fossil fuels are rapidly depleting, the world is turning more to Geothermal as a renewable, green, source of energy. Equally, conversion technologies for low enthalpy geothermal sources to electricity are being more widely adopted and Hot Rock (or EGS) wells are being explored as energy sources for geothermal electricity production. The incidence of dissolved mineral deposition is becoming more of a limiting design and operational issue. The importance of deposits such as silica, arsenic sulfide and antimony sulfides, their impact and prevalence in low temperature energy extraction technologies such as binary plants or multiple flash systems are now becoming essential factors for consideration. Whilst silica and silicate chemistries are well researched, documented and understood, there is little available research on the sulfides of arsenic and less on the antimony complexes, especially on mitigation strategies (Brown 2011). Accordingly the increasing incidence of these deposits limiting power production is a problem requiring research, analysis, interpretation and, more importantly, solutions.

The main options for preventing scale in the surface and reinjection systems have, historically, been limited to (i) maintaining a brine temperature that prevents the silica saturation index from exceeding 1 or (ii) addition of acid to lower the pH and (iii) lowering the temperature only to a point where the silica saturation index does not exceed equilibrium solubility. To achieve (ii), the spent brine is often acidified to pH<5 which can cause severe corrosion issues. Another option is to remove silica from the brine by the Crystallisation seed Recycling Clarification (CRC) process. Some of the geothermal plants in the Imperial Valley USA use the CRC process to remove silica, but at a very high capital and operational cost. Recently, there have been reports (Gill 2011) regarding the development of silica inhibitors.

The incidence of antimony sulfide compounds causing concern in binary plant operation and design has been well documented in the Habanero Enhanced Geothermal System (EGS) field near Innamincka Australia and at the Rotokawa and Ngawha sites in New Zealand. As geothermal prevalence progresses, low enthalpy energy recovery systems such as additional flashes and binary units are being implemented. As a result deposition from silica, antimony and arsenic compounds are becoming more of an issue for efficient sustained geothermal energy conversion to electricity.

Addison and Brown (Addison, Brown, 2012) documented the in-depth process of determining optimal design parameters to prevent the deposition of these compounds in the binary plant at Ngatamariki. The object of this process was to balance energy extraction against power production while preventing deposition from occurring. Whilst this is an effective way of preventing deposition it also comes at a cost; a four degree increase in the outlet brine temperature of a binary plant from 90 to 94 ^{o}C can decrease production capacity by 10%. However as Brown, 2011 noted; “to date there had been no successful chemical treatment for antimony sulfides (stibnite) and that present options for remediation include caustic soda washing, steam cleaning and mechanical removal”. The plant operators and, at an earlier stage, the designers, are left with the option of progressively losing efficiency as scaling occurs and the ongoing costs of chemical (usually caustic) cleans, hydro blasting and disposing of the hazardous wastes, or, designing the plant to operate at temperatures above which the compounds deposit. Since Brown’s publication, Gill (Gill, 2010, 2012) conducted laboratory tests on a range of commercially available products, including a newly developed copolymer product that demonstrated successful threshold and dispersion impacts on stibnite.

Given the significant financial returns, improved safety and better environmental practice of keeping antimony and arsenic compounds in solution through a binary plant to reinjection, it was decided to field test the product. A plant that has a known and significant stibnite deposition issue was used for the trial. The two phase Ormat units consist of a vaporizer followed by six preheaters. Stibnite deposition is found on all brine side units varying in color from black, grey through to red indicating both crystalline and amorphous antimony sulfide is depositing. Analyses of deposits from the separators and reinjection pump impellors indicated that the scale was essentially pure antimony sulfide. Whilst deposition on impellors is likely to be a result of pressure changes and turbulence across the impellor surface, it still is significant enough to impair reinjection pressures after a few months. Suffice to say the operational balance of this plant is critically dependent on the stibnite deposition and so it makes a good candidate for the side-stream onsite trial.

1. THE TEST SITE

Top Energy Limited is the local electricity generation and lines network company which supplies 30,000 electricity consumers in the far north of New Zealand's North Island. The plant is a binary plant producing 25MW from three OEC units. The geothermal fluid is two phase and the vaporisers receive both steam and separated brine. Condensed steam is remixed into the preheaters for further energy extraction. As has been well documented (Brown, 2010) antimony sulfide creates many operational constraints and problems that require close management. The net result is antimony sulfide deposition is one aspect that prevents the plant running continuously at maximum efficiency. Although the antimony levels are under 1.4 ppm the saturation index is such that the plant must operate within strict parameters. As always there is a trade-off between operating parameters (reinjection and binary temperatures) and efficiency. Accordingly each OEC is mechanically cleaned yearly and the two smaller units chemically cleaned approximately each quarter. It is well accepted that antimony sulfides require careful handling and special disposal. Chemical and mechanical cleans therefore are costly and a process to be avoided if at all possible.

Antimony sulfide, and more specifically stibnite, the crystalline form, deposits throughout the Ngawha plant system. As antimony sulfide deposition mainly depends on temperature it is also influenced significantly by pH (Brown2010) (Gill, 2011). Accordingly antimony sulfide deposits begin forming in the vaporiser and continue throughout the preheaters. It is noted that the reintroduction of condensed steam into the vaporiser causes a pH drop and again increases the stibnite saturation index (SI). Further downstream deposition on reinjection impellors is shown to be near pure stibnite by XRF and XRD analyses. This shows that at the reinjection temperature the SI is still critical and any change in pressure will cause deposition. This makes reinjection pumps, bends, valves and the slots in reinjection casings potential problem points. In many cases reinjection can also be a plant limiting parameter. Preservation of reinjection permeability and flow rates is also extremely important to the geothermal development.

This paper documents a series of onsite, pilot scale, heat exchanger tests. Pilot heat exchangers were used so that the exchangers could be thoroughly examined via destructive analysis. Preliminary site tests indicated that the selected product had a discernible impact on the deposition of stibnite (Gill, Rodman, and Muller 2013) but additional onsite test refinement was needed. In addition, the objective of this paper is to highlight some of the chemical treatment options available to address many of the issues related to corrosion and scaling, especially antimony sulfide and silica so that more energy can be extracted from the produced geothermal brines.

1.1 Experimental

The test rig needed to be simple, yet flexible enough to accommodate a range of plant scenarios. It was envisaged from the outset to be used for silica, metal sulfide and corrosion tests where plant parameters could be replicated within reasonable limits and ongoing iterative changes easily made. A large fixed piece of apparatus was not considered as portability and a high level of adaptability was required. The net result was a base model test rig that has become affectionately known by the team and site engineers as “The Crab Cooker” (Figure 1).

Figure 1:- Basic, adaptable, test rig used for trials. Also known as the "Crab Cooker".

After each test run, the sample coils carrying the brine were removed, sectioned and analysed. Temperatures and flows were recorded by shift engineers and after each test run of typically 2-3 weeks the control parameters and control mechanisms were reviewed and refined. This iterative process provided some interesting and informative results but finally resulted in an experimental rig that closely mimics the brine temperature gradients in the binary plant, the length and metallurgy of the exchanger coils, the low end temperature of pentane entering the plant and a brine flow in the test coil of 1m/s compared to 2m/s in the final preheater. A lower velocity in the tubes was expected to exaggerate the stress on the system and result in increased deposition.

The test rig essentially consists of two coils immersed in a cooling vessel. Flows through the coils can be varied as can the amount of cooling water through the cooling vessel. Temperatures and pressures are recorded for the incoming brine and, after the flows split into the two feeds for each coil, again on the outlet side of these coils. Due to the supersaturation of stibnite in this brine, care was taken to size the piping to minimize any sudden pressure changes and prevent throttling upstream of the test coils. Accordingly the flow control valve for each coil is well downstream of the test coils.

The initial and final tests were sent for third party independent SEM and EDX analysis. The data from the EDX was normalised using the simple mathematical equation of “EDX % for 2mm spot X total weight of deposit in g/kg of pipe” to provide results expressed as “g element /kg of pipe”. This minor data manipulation was required for the test 4 data, as there was some corrosion of the interior of the control test sections during transportation to the laboratory.

1.2 Results and discussion

1.2.1 Test One:

Conditional saturation index (SI) is defined by the ratio of ionic product of antimony and sulfide to the ionic product of antimony and sulfide at equilibrium for the experimental conditions. Given the, essentially logarithmic, variation of the saturation index with temperature for stibnite (Figure 2) and the observations that the deposition of stibnite varies with temperature and pH (Brown, 2011) the first test was carried out to determine some proof of concept of the impact of the copolymer compound on the formation of antimony compounds. Two 4 m long mild steel coils were used and the temperature controlled by varying the cooling water flow manually. The copolymer product was dosed at 30 ppm into one coil based on the estimate of the initial flow in the coils. For this initial test, the outlet of the test rig was returned directly to the reinjection line and the flow estimated using the pressure drop between the inlet and outlet of the coils. The second coil was left untreated as a control. The test was run for 21 days with an initial, estimated, flow of 150l/hr through each coil.

During the course of the experiment, it became apparent that it was necessary to develop a better way of controlling and measuring both the flow and temperature of the brine in the test coils. Despite the best efforts of all involved to control the temperature of the cooling water to be 75°C and flows through the coils to be 150L/hr, it was noticed that over the period of the trial the flow steadily decreased and the cooling water temperature decreased substantially. On two occasions the flow to the coils ceased, but product was still added and therefore built up in concentration in the treated coil. A heat balance on the coils in week three of the trial indicated the flow had decreased to approximately 50L/hr, meaning that the brine temperatures would also have dropped significantly below the desired target and the flow further restricted and eventually stopped.

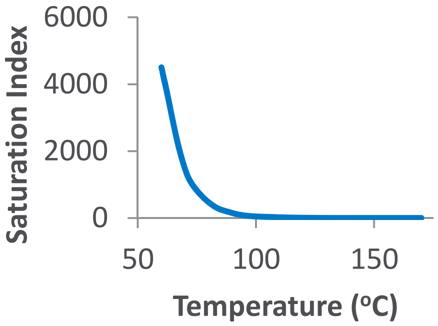

Figure 2:- Saturation indices for stibnite (pH 7.65, Sb 1.84ppm, H_2S 25ppm)

Figure 3:- The locations at which the coils were cut for subsequent analysis.

Figure 3 shows the coil before it was cut and the deposit weight analysis for the sections is shown in Figure 4. What is clear from the results shown in Figure 4 is that the copolymer had an effect on the deposition of antimony, such that the deposition was essentially delayed but not completely eliminated. The untreated coils had a consistent, even and increasing quantity of antimony deposition with no carbon present whereas the treated coils had white deposits that steadily decreased through the coil and contained significant quantities of carbon and silica. It was assumed that the presence of the carbon was likely to be due to product deposition that resulted from overdosing when the brine flow through the coils was interrupted.

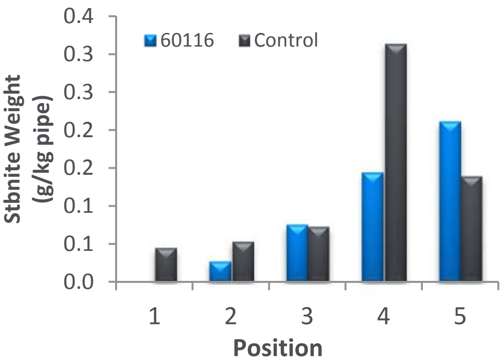

Figure 4:- Deposit weight at various sections of both untreated and treated coils.

Based on these results it appeared that the product was modifying and decreasing the deposition of antimony as desired, however, there was too much noise in the experimental procedure to allow any firm conclusions to be made. It was decided that the control of flow and temperature needed to be improved and to be more consistent with those experienced in the plant. The presence of high concentrations of silica and appearance of arsenic sulfide in the deposits supported the theory that the brine temperature had been consistently well below the target temperature of 85°C, and was likely to have dropped to approximately 40-50°C.

The next two tests were conducted with improvements to the rig, including automated temperature control via a solenoid valve and controller, more accurate flow control through the coils and an increase in flow to 300L/hr. The test coil length was also increased to 11 metres which is the same length as the preheater tubes and, in the final iteration, the cooling water was recirculated and the temperature controlled to 75°C +/- 1°C, to more closely approximate the process side temperatures in the plant.

In each of these tests there was noticeable increase in the amount of deposition observed and both dose rate and duration were altered.

1.2.2 Test Four:

Two coils were set up with flows of approximately 300L/hr each, one treated and one control coil. The treated coil was dosed with 8 ppm of an organic silica inhibitor and 8ppm of the copolymer product. After 15 days the coils were removed and, when examined, showed a noticable difference in the cooler part of the coils. An even deposit, that had an appearance consistent with antimony sulfide, was observed in the untreated coil but appeared to present to a much lesser extent in the treated coil, with several bare patches of the tube still exposed. It was also noted that the brine flow to the treated coil did stop for approximately 12 hours but the product dosing did not. As with the first trial this is likely to be the cause for the white deposit.

The temperature of the cooling water was controlled to 75°C +/- 0.1°C for the duration of the trial. The plant operators checked the operation of the test rig during most shifts and made adjustments in an attempt to maintain the brine flows through the coils constant at 300L/hr. However, the brine flow did vary, meaning that the brine outlet temperature also varied between 79 and 95°C. Despite this variability, the temperature was predominantly maintained at approximately 85°C (Figure 6), which was lower than the 93°C control target for the plant. The intention of this trial was to target a brine temperature of 85°C, which was significantly lower than that observed in the plant, to ensure that the deposition of stibnite would not simply be moved further along the reinjection line. While the brine temperature in the test coil did start higher than the control, there were periods where the test coil temperature was recorded to be well below the average (Figure 6). As demonstrated in Figure 2, the saturation of the stibnite would have been substantially higher at the lower temperatures.

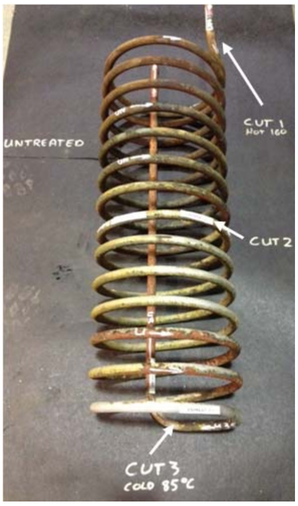

Figure 5:- Coil from test four indicating the locations at which the sections were removed for analysis.

Figure 6:- Manually recorded coil outlet temperatures

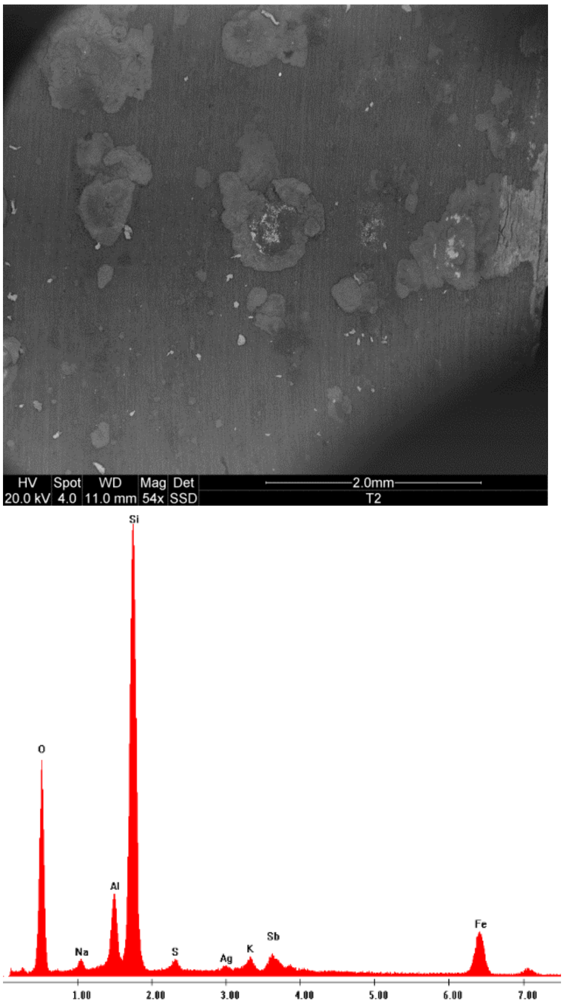

Figure 7:- Treated coil section 2 electron micrograph and associated EDX

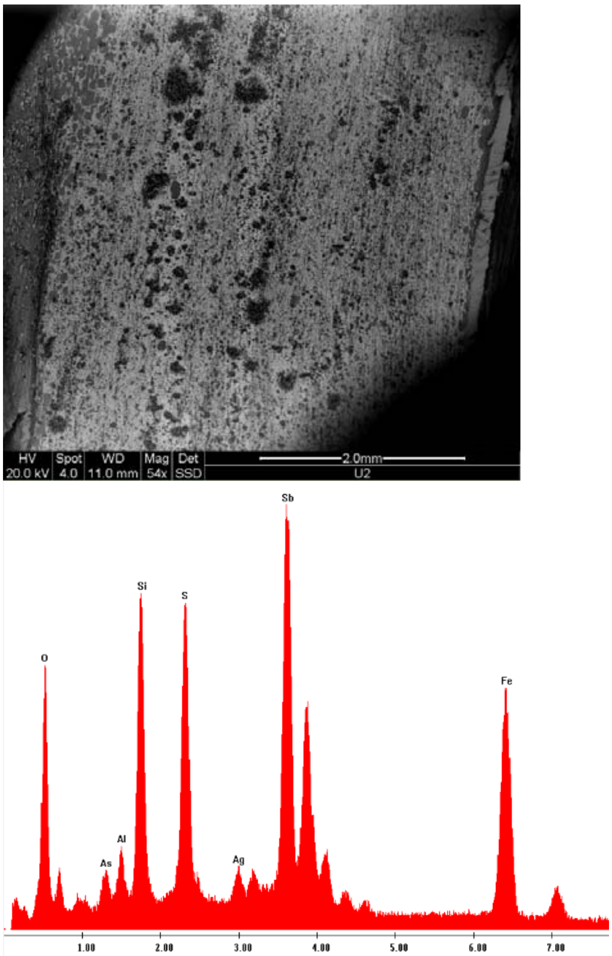

Figure 8:- Untreated coil section 2 electron micrograph and associated EDX

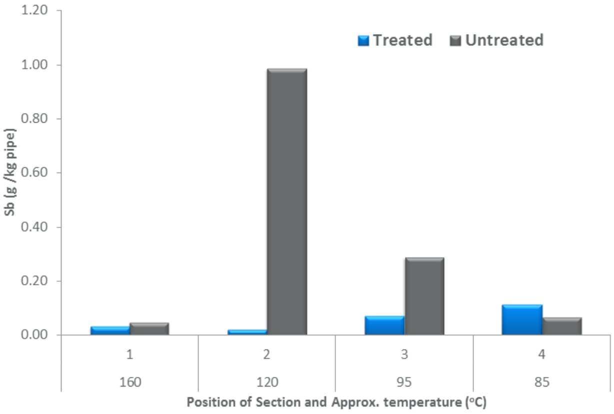

Figure 9:- Comparison of antimony deposition in the treated and untreated coils.

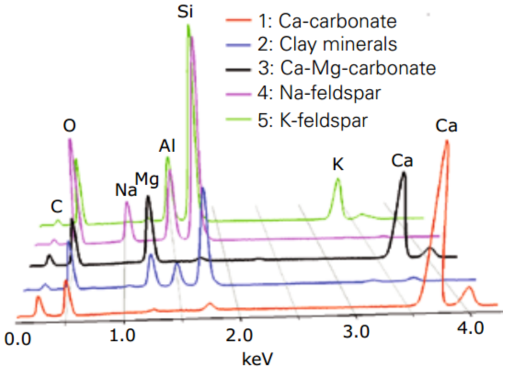

Figure 10:- Example mineral EDX scans showing similar profiles for the Na and K-feldspars as that shown in the EDX for the deposits in the control and treated coils.

As expected, the results from test four show that the antimony deposited rapidly as the temperature was reduced in the untreated coil (Figure 9). The peak in antimony deposition at position 2 was likely to be the result of the rapid oversaturation of antimony sulfide and subsequent reduction in antimony concentration leading to lower momentary excesses being experienced in the cooler sections of the coils. Much less antimony sulfide was deposited in the treated coil, indicating that the copolymer had a significant impact on the deposition of antimony. The slight increase in the deposit density in section 4 is likely to be due to the very high saturation index and large momentary excess at that point which was not able to be controlled by the copolymer. The occasional reduction of flow and, subsequent decrease in temperatures, in the treated coil would have resulted in occasional massive increases in the saturation index, far exceeding the capability of the copolymer to maintain the stibnite in solution.

The data suggests that silica was deposited at almost equivalent rates in the untreated and treated coils, but the EDX data indicates that the silica that is being deposited is likely to be sodium and potassium feldspar clays as shown by the presence of sodium, potassium and aluminium along with the silica in the spectra at ratios that are similar to that shown in scans of pure substances (Figure 10).

Previously published results (Gill, et al., 2010, 2011 and 2013) on the development of various inhibitors to control calcium carbonate, calcium sulfate, silica, antimony sulfide, and corrosion has documented the use of these inhibitors, in various geothermal fields, to provide increased power generation and for protecting assets.

CONCLUSION

In the final set of results a significant reduction in antimony sulfide deposition was recorded. The results show that deposition has not been simply transported to a cooler region of the plant as the test conditions, with respect to stibnite saturation, were kept well above those of the reinjection lines. The test rig is able to simulate binary heat exchanger system with a precise control of delta T. This side stream rig demonstration eliminates any risk to the entire plant. However, these results should help in planning and executing a full plant trial to further demonstrate the efficacy of the chemical treatment.

The work presented in this paper demonstrates that it is possible to minimize stibnite deposition, along with silica, to help generate more electric power using binary units operating at a much cooler temperature than is currently used; or it will be possible to operate at the design load of the plant longer between cleans which is equivalent to increasing capacity. This demonstration, moving from the static laboratory testing to field evaluation clearly indicates the validity of the laboratory study. The results are extremely encouraging for a full plant trial.

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