STIBNITE CONTROL IN ORMAT BINARY UNITS: PREVENTION AND ONLINE CLEANING

Logan Muller[1], Jasbir S Gill[2] and David Rodman[3], Kevin Brown[4], Ray Robinson[5]

[1]Dr Logan Muller. Nalco 2A Pacific Rise Mt Wellington NZ

[2] DR Jasbir Gill. Nalco Naperville USA

[3] Dr David Rodman Nalco Townsville Australia

[4] Dr Kevin Brown. GEOKEM Christchurch NZ

[5] Ray Robinson TOP Energy Kaikohe NZ

Author lmuller1x@nalco.com

Keywords: *Stibnite inhibition, Metal Sulfide cleaning and inhibition, ORMAT Binary*

ABSTRACT

At last year's NZGW an update was given on the trial work under way at TOP Energy on the chemical control of stibnite and the other morphologies of antimony sulphide.

This paper explains the results after one full year of operation and the chemistry behind keeping Antimony Sulphide from depositing.

Since 2008 station one's OECs needed to be shut each 12 weeks for a caustic clean and sometimes a water blast or drilling to remove the deposited antimony Sulphide (referred to as Stibnite from here on). The trial OEC has now run a complete year without the need to shut. During the program it was discovered that the brine pH of another OEC unit was one and a half pH units lower than the others. The treatment used here at the same dose rate did not prevent the deposition but did change the morphology of the deposit. This change became the focus of how we could achieve online stibnite removal. Varying dose rates were used and the resulting deposits analyzed. It became apparent that the carboxylate groups of the copolymer were acting as super plasticisers and when dosed far enough ahead of the unit were transforming the crystalline and amorphous stibnite into colloidal gels.

These gels were far easily removed and although it was not cost effective to completely inhibit the stibnite in the lower pH (SI climbing from 27 to 144) the deposit was softened to a point where the velocity in the final preheaters was enough to self-clean. The net result being efficiency was kept high on preheaters 1,2 and 3 and 4 self-cleaned leaving the plant efficiency high enough to keep running and avoid having to shut for cleaning.

1. INTRODUCTION

Low enthalpy extraction technologies are being adopted as the return on capital investment in geothermal extraction shifts to be more favourable. In two phase steam systems a steam turbine is sometimes followed by a binary plant that uses the brine and low pressure steam separation to generate additional electricity. Whilst the conversion is not very efficient the binary technologies allow additional energy extraction and power generation. The similarities in the issues these technologies have to EGS are the control of more unusual compounds such as metal sulfides and silicates and corrosion.

Ngawha Generation is known to be one of the binary plants that has the most severe stibnite issues in the world. Careful design and meticulous plant operation have meant that the OEC units need to be taken offline every 12 weeks for a caustic clean and once or twice a year for high pressure waterblasting or drilling to remove hard deposited stibnite.

Side stream test rig trials have led to a full scale trial. After 12 weeks of operation it was evident that the treated unit was remaining clean and the untreated control unit) fouled in the historical pattern.

After 11 months of operation the treated unit is still producing at above historic capacity and what was the control unit is now being treated. Furthermore recent tests have shown that units' performances can be enhanced whilst still in operation by using online cleaning techniques. This is explained in this paper.

This paper describes the journey, the results, the chemistries and potential future applications of this breakthrough

2. THE ISSUES

Deposition of silica, antimony and arsenic compounds is significant enough to warrant serious investment in complex test plants prior to investing in the construction of binary generation plants. Addison and Brown (Addison, Brown, 2012)[1] document the in-depth process of determining optimal design parameters to prevent the deposition of these compounds in the binary plant at Ngatamariki New Zealand. The object of this process is 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, where a four degree increase in the brine discharge temperature of a binary plant from 90 to 94^{o}C can cost 10% of production capacity. However as Brown, 2011[2] 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 operation and, at an earlier stage, design is left with the option of progressively losing efficiency as scaling occurs and the ongoing costs of chemical (usually caustic) cleans, hydro blasting, downtime, and disposing of the hazardous wastes, or, designing the plant to operate at temperatures above which there is no fouling of the exchangers. pH adjustment is becoming common in plants where acid is used to prevent silica deposition in reinjection lines and wells but this is neither appropriate when antimony sulfide exceeds its equilibrium solubility nor has the longer term effects of significant acid reinjection into the aquifer been thoroughly researched. Corrosion can be a significant cost in assets under acidic operating conditions.

The Ngawha generation plant is unique in that it has many of the metal sulfide, calcite and silica issues that are being faced in the aforementioned technologies. Careful management and expert input from GEOKEM have enabled the plant to find operating parameters to stay in production and in fact expand operations. First commissioned in 1998, subsequent scientific investigation showed the plant's output could be expanded without affecting Ngawha's geothermal field reservoir pressure. So in 2003, the Company began to push forward with its Stage 2 expansion plan with a capacity of 25MW. Silica, arsenic sulfide and antimony sulfides limit the total output of the plant and as with Ngatamariki the design and subsequent operation revolves around these parameters.

Since 2008 the plant has needed to take an Ormat Energy Converter (OEC) Binary unit offline approximately every three months and remove the stibnite deposits using caustic cleans. The antimony sulfide sludge is concentrated then trucked off site for treatment and disposal.

The antimony sulfide deposits are both crystalline or “stibnite” and in the amorphous antimony sulfide (“metastibnite”) states. Whilst the deposition is predominantly in the binary preheaters a steady decline in the capacity of the reinjection wells was experienced.

The operations team regularly forced higher pressures down the reinjection wells which temporarily improved reinjection rates. However the ‘bounce back’ periods kept on shortening and this approach was becoming less applicable. The other potential courses of action were to incrementally reduce plant capacity, caustic clean the reinjection wells, or invest in an extensive capital project to connect a new reinjection well.

The risks associated with each one of these options are significant. Reduction in plant output to operate within the limits of the reinjectability means reinjection pumps are constantly running at near trip pressures and amperages and the ongoing cost accumulates as power production reduces. The option of caustic cleaning the well means the well must be taken offline, costing generation capacity and runs the risk of precipitating calcite downhole potentially worsening the problem. Connecting another reinjection well is a significant capital expense and neither offers a quick nor sustainable solution. The modelling for the cost benefit analysis is not straight forward as the rate of loss of reinjection is nonlinear.

In all of the solutions above, none actually stop the root cause of the issue: deposition is affecting the long term performance of the reinjection wells, as the wells continue to lose injection capability.

The challenge of dealing with antimony sulfide left the plant with operational controls only to mitigate the impact of plant performance as there was little research nor chemical solutions to inhibiting its formation The solution was to pull the metal sulphide and silica knowledge of GEOKEM and the experience TOP Energy has gained in the way it manages the physical processes of the plant to mitigate deposition problems together with the research, international Geothermal experience and polymer development capability of Nalco.

This collaborative approach has shown to produce some important advancements for the industry.

3. CHEMICAL APPROACH

Calcite inhibition is relatively commonplace and the mechanisms of threshold inhibition and dispersion are often employed. Historically these have been low molecular weight polyacrylates. However these have been shown to be ineffective against the deposition of the metal sulfides and silica and traditional polyacrylates can form Calcium Acrylate deposits in Binary units. Increasing the risk of further fouling in a binary unit is best avoided if possible. A standard threshold inhibitor of a proprietary polyphosphonate was lab tested on antimony sulfide but it was not effective against preventing its deposition. This performance comparison is based on the authors' definition of threshold inhibition, where particles <0.2 microns are considered soluble antimony. Based on these results, it brings credence to the hypothesis that for highly insoluble salts such as antimony sulfide, certain polymers with high anionic charge density are very effective in reducing the particle size and imparting negative charge to the precipitating particles and therefore are more effective than traditional threshold inhibitors such as phosphonates. It is thus quite challenging to inhibit the formation of minerals with extremely low equilibrium solubility and for such minerals the best strategy to mitigate fouling is to accept the precipitation but modify the characteristics of the precipitated particles.

Compounding the issues of antimony in Geothermal applications is the ability to test and quantify colloidal forms of antimony in brine. Acidic digestion is a method referred to by Onishi[5] (Norman ,1998) but the efficacy of colloidal measurement is only referred to in its uses in tracing in human diagnostics. However it is the formation of colloidal antimony sulfide that seems to be leading to the successes in inhibition and removal referred to later in this paper.

A three pronged approach was lab tested where a combination of chelation, threshold inhibition and dispersion was employed. The lab results were promising.

Based on the lab results a side stream test rig was built to test the chemicals in situ using actual brine.

4. TRIAL RIG RESULTS

A small test rig was constructed with two test coils cooling the incoming brine to 80°C off the main brine supply line to the Ormat binary unit. One was dosed with the polymer and the other left as a control. After a month the coils were destructively tested by GEOKEM. The findings are depicted below and discussed in the paper "Maximising Geothermal Production by Controlling Scale and Corrosion in Geothermal Systems" [3]

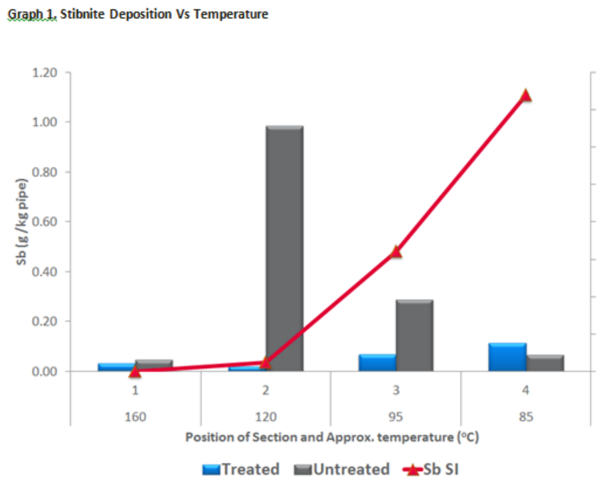

Figure 1: Stibnite Deposition Vs Temperature in Centigrade

Based on these results a plant trial was initiated. The results of which are discussed below.

5. PLANT IMPACTS

There were several changes noted in the plant. These are discussed under the following headings.

1. Temporary increase in soluble calcium levels
2. Increase in capacity of reinjection wells
3. Significant reduction in fouling rates of the binary units.
4. Change in the physical characteristics of deposits.
5. Ability to soften and remove old deposits whilst in production
6. Increased power output

5.1 Temporary increase in Soluble Calcium levels

The plant had been using a traditional polyacrylate for several years for the control of calcite. This had been keeping the wells at full flow and pressure since 2008. However once the copolymer was used downhole the soluble Ca levels in the brine increased indicating removal of Ca from the downhole system. The soluble Ca levels decreased to initial values after a month but it showed the chelation/dispersion/threshold inhibition of the copolymer was successful in dissolving calcium deposits. Additionally there was a decrease in the pump pressures needed to dose the inhibitor and a reduction in overall cost of 50% for the calcite inhibition.

The graph below depicts the soluble Ca levels.

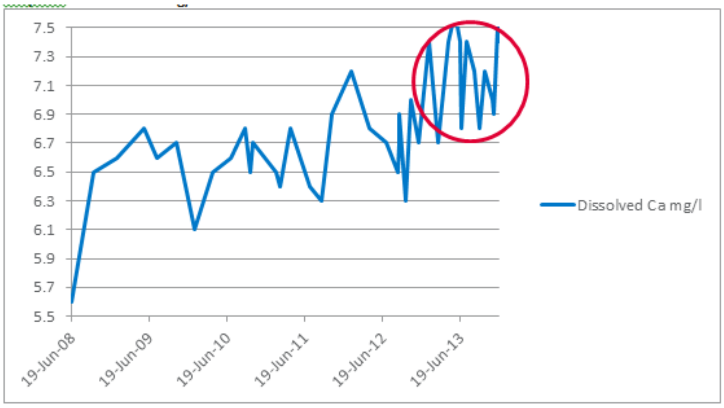

Figure 2: Dissolved Ca mg/l Vs Time 1

5.2 Increase in Capacity of Injection wells

This is best shown graphically.

The first diagram shows the steady decline of capacity of the reinjection wells. This decline was at the point of reducing plant capacity. According to the independent consultancy GEOKEM the loss of reinjection capacity was due 'probably to the build-up of silica or antimony sulfides in the casing or immediate reinjection zone of the aquifer'. The probable chemical processes behind this are discussed in the 'Discussion' section.

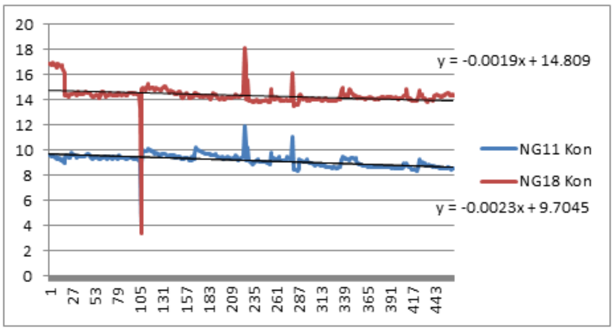

Figure 3: Kon Vs Time April 1 to June 30

The relationship between flow and pressure was used and recorded as Kon. For turbulent flows between a Reynolds number of 3000 and 10000 the flow pressure relationship is relatively constant at the given roughness and diameter of the reinjection lines and reinjection well casings at Ngawha. Therefore this flow pressure ratio was monitored during the trial and is referred to as Kon. Over a time frame of months it was easy to see the reduced pressure needed to inject similar or increased quantities of brine. The Kon was used as a parameter to detect trends during the trial periods only.

After dosing the copolymer at 4 ppm for two months it was observed that the decline in injection capacity (a declining Kon value) stopped and, in fact, the well increased in capacity. It was decided to conduct a short period high dose (from 4 ppm to 30ppm) for five days in early October. The following was observed:

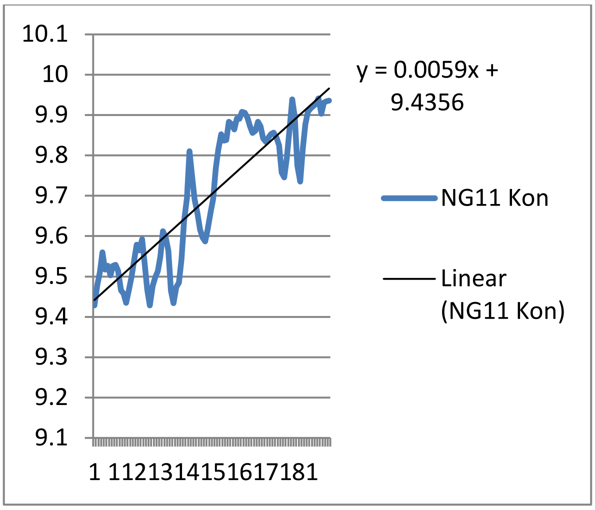

Figure 4: Kon Vs Time During Online Clean 1

Since June 2013 the well has recovered from a declining rate of 146t/hr to now an increasing capacity of 222t/hr at lower injection pressures. This reduction in pressure directly impacts the parasitic load on the plant as the injection pumps are running at lower amperages to achieve the desired injection rates and avoids the need for investing in new reinjection wells.

5.3 Significant Reduction in the Fouling Rates of the Binary Units

As documented earlier, each binary unit needed to be taken off line and cleaned due to antimony sulfide fouling. This was done every 12 weeks or so. Pressure differentials would increase to over 3 bar across the preheaters at which point the decreased brine flow would impact power generation capacity.

The online trial was carried out on two identical 6 MW units side by side. One was treated and the other not.

The following graph shows how the pressure differential climbed, as per usual, across the untreated unit (shown in blue) but not across the treated unit (shown in red). The slight rise in the treated unit is a result of more flow being forced through the treated unit as the untreated one fouled. After five months the treated unit pressure differential is still 0.73 bar.

The savings in cleaning costs and plant performance loss are significant and reducing the need for manual cleaning and disposal of the toxic waste is a health and safety gain.

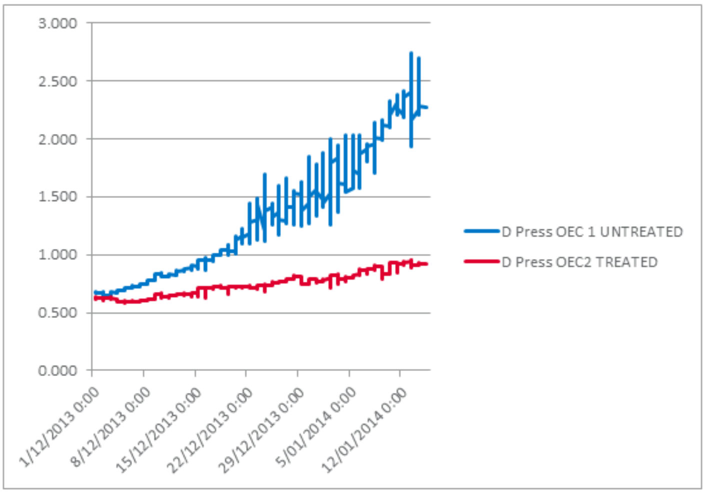

Figure 5: Pressure Vs Time. Treated and Untreated

5.4 Change in the physical characteristics of deposits.

Stibnite is a solid crystalline deposit. It usually forms in the area where the rate of deposition is slower, which enables the crystal lattice to form. This situation typically occurs in the warmer preheaters. The crystalline stibnite is difficult to remove even 22,000psi water blasting leaves 'tracks' in the deposit. Even though crystalline stibnite is relatively soft (mohs hardness of 2) if it co- deposits with silica it can be extremely difficult to remove (Brown 2011). Specially tooled drills are used if complete removal is needed.

As we follow the brine path through the preheaters the deposit becomes the metastibnite form of predominantly amorphous, colloidal, antimony sulfide which will transition through a dark grey to red colour. This too will precipitate onto the process cooled mild steel of the preheaters and requires high pressure water blasting to remove. Typical deposits are hard silver black or red deposits as shown below.

Figure 6: Classic crystalline stibnite

After the online test it was noted the deposits had become softer and more "pasty". These deposits were easier to remove and have led to the prospect of performing online cleaning using the copolymer. At the time of writing, promising initial results have been obtained and are the focus of further collaborative work.

The pictures below show how, even low doses of, the copolymer can cause the deposit to become a thick soft paste (Fig. 6). After a high level, shock, dose the deposit became a pasty, almost gelatinous, crimson red deposit (Fig.7) instead of the usual hard grey/black. These gelatinous deposits have become a focus in advancing the potential to remove existing stibnite deposits and are discussed in the section below.

Figure 7. Soft paste-like deposit after dosing 4 ppm

Additionally, the colour of the reinjection line strainers and lines changed significantly. For years the strainers have always had a light black stibnite deposit with occasion flakes of stibnite that have come off the several kilometres of pipework. Since using the copolymer the strainers have taken on a crimson red further indicating a change toward colloidal metastibnite. Reinjection gate valves are now far easier to close and open showing a decrease in fouling and deposits on valve seats and slides.

5.5 Ability to soften and remove deposits whilst in production

Given the changes in characteristics of the antimony sulphide a short trial was run on one OEC where 25 ppm of the copolymer was added for 24 hours. The total pressure only changed slightly, however the pressure dropped noticeably across the exchangers immediately downstream of the dosage point.

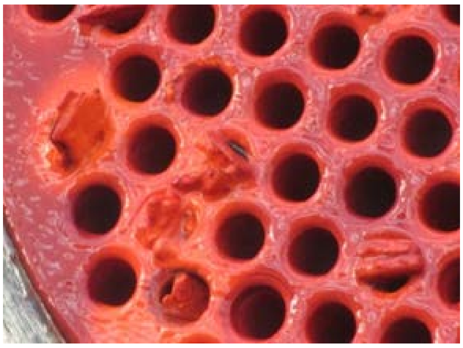

Figure 8. Soft paste-like deposit after dosing 20 ppm

Given the changes in the consistency and morphology of the antimony sulphide a test was conducted by purging three 30 second bursts of steam into the fouled unit. The results are depicted graphically below from the plant scada. These show the deposits being moved out of the exchangers, decreased resistance to flow, increased t/hr of brine and most importantly improved power output.

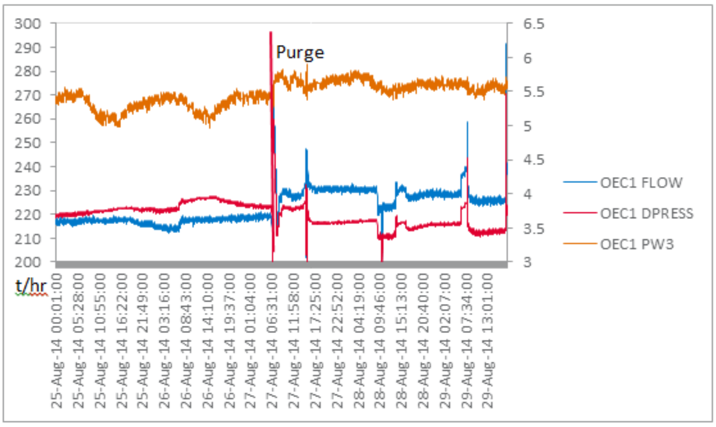

Figure 9. Online purge shows increased power out put

5.6 Increased power output

Whilst the specific megawatts are commercially sensitive the plant output has been higher than historically. The two reasons postulated for this are the increased cleanliness of the binary preheaters and where deposit is occurring it is in the gel like form whose thermal conductivity is higher than the hard historic scales encountered.

6. DISCUSSION

It appears the combined action of threshold inhibition, chelation and dispersion has altered the way in which the antimony sulfide forms. As documented in GRC Transactions, Volume 35 (Gill 2011)[4] the method for controlling these metal sulfide deposits was to allow the amorphous particles to form then keep them small enough to be dispersed or chelate them onto a larger negatively charged polymer chains preventing crystal structures to form. Achieving a less dense, more voluminous, deposit allows it to be carried through the plant without depositing.

The observed impact on existing deposits is postulated to occur via a similar mechanism whereby the deposited antimony sulfide and silica in the reinjection wells was predominantly amorphous in nature and hence able to be transported due to the chelation and dispersion properties of the copolymer. After deposition occurs in the preheaters the temperature remains relatively stable through to the reinjection wells and increases as it re-enters the aquifer. As the skin temperatures of the preheaters remain lower than the brine temperature there is no temperature induced deposition in the reinjection lines. However it is noted that deposition occurs at any point where there is high shear forces like pump impellors, bends or throttled valves. As a result of the rapid deposition, the silica and antimony sulfide form amorphous deposits that are able to be penetrated and subsequently dispersed by the polymer. This is the mechanism that is thought to have led to the recovery of reinjection capacity from 146t/hr to 222t/hr.

The mechanism above applies to antimony in the brine solution. However removal of deposited crystalline stibnite has been also investigated. Initial results have shown that deposits can be removed from binary exchangers. This creates another tool available for plants where stibnite deposition is a problem. The synergistic effect of the carboxylates and carboxylic acids seem to have a compounding effect more so than any single chemical on its own.

Whilst yet to be determined we are working on the premise that the dissociation of the carboxyl groups are forming polar yet overall negatively charged carbon chains. This deprotonation of specific molecular weight carboxylic acids and poly carboxylates is what seems to be strong enough to remove the antimony from its crystalline lattice. Once detached the strong anionic side chains are enough to keep the removed antimony compounds in suspension. The high Zeta potential of the copolymer is, at higher dosages, keeping the antimony sulphide in colloidal form. This would explain the gel-like bright crimson-red nature of the deposits after high dosages of the copolymer. These characteristics; degree of polarity, anionic charge and deprotonation may account for the difference in lab performance between the copolymer structures of the polycarboxylates and traditional polyacrylates used in the geothermal industry.

7. SUMMARY

The collaborative approach combining specific chemical knowledge, geothermal experience, operational experience, research and development capacity was used to solve some significant challenges that face the growing geothermal industry. The inhibition of stibnite deposits and the option of metal sulphide removal without the need to shut and clean a plant is now achievable for many plants. The glue that held this collaboration together and motivated the parties is a genuine interest in moving the geothermal industry forward.

The challenges before us to find sustainable energy are too great to tackle in isolation or in disparate silos of company self-interests. If, as a progressive society, we want to mitigate the impacts of climate change and develop new long term energy provisioning now is the time to pull our resources together.

REFERENCES

Addison, S. and Brown, K.: Ngatamariki Test Rig. . *Proceedings 34th New Zealand Geothermal Workshop.* (2012).

Brown, K.: Antimony and Arsenic Sulfide Scaling in Geothermal Binary Plants. *Proceedings Int Workshop on Mineral Scaling.* (2011).

Gill, J., Rodman, D., Muller, L., Brown, K. and Robinson, R.: Maximising Geothermal Production by Controlling Scale and Corrosion in Geothermal Systems. *Proceedings 35th New Zealand Geothermal Workshop.* (2013).

Gill, J.: *GRC Transactions, Volume 35 (2011)*

Onishi, H, 1998. The Chemistry of Arsenic and Antimony. *Ed Norman, N.C. Springer*